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PROCEEDINGS OF THE HIGH ENERGY DENSITY MATTER (HEDM)
CONFERENCE HELD IN R. (U) AIR FORCE ASTRONAUTICS LAB
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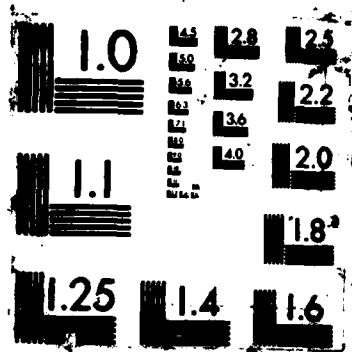
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Proceedings of the High Energy Density Matter (HEDM) Conference

Held 12-13 May 1987 in Rosslyn VA

September 1987

**Editors:
W. J. Lauderdale
W. A. Sowell**

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**Air Force Space Technology Center
Space Division, Air Force Systems Command
Edwards Air Force Base,
California 93523-5000**

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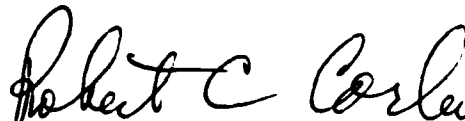
FOREWORD

This is the conference proceedings of the High Energy Density Matter (HEDM) Contractor's Conference held 12-13 May 1987 in Rosslyn, VA. AFAL editors were 1Lt Walt Lauderdale and Capt Bill Sowell.

This conference proceedings has been reviewed and is approved for distribution in accordance with the the distribution statement on the cover and on the DD Form 1473.


WALTER J. LAUDERDALE, 1Lt, USAF
Project Manager

FOR THE COMMANDER


ROBERT C. CORLEY
Chief, ARIES Office

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The High Energy Density Matter (HEDM) Contractor's Conference was held 12-13 May 1987 in Rosslyn, VA. It provided HEDM researchers an opportunity to become acquainted with the work of their colleagues in this area. The speakers were researchers who had been under contract by October 1986. In addition, presentations on Air Force in-house research were made by the Air Force Astronautics Laboratory (AFAL) and the Air Force Aeropropulsion Laboratory (AFAPL).</p>					
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11. Contractor's Conference, 1987 (U)

18. H_2 , hydrogen, He_2 , spin-orbit, spin-spin, multi-configuration self-consistent field, MCSCF, condensed phase, metastability, quantum Monte Carlo, trial function, polyatomic hydrogen, ions, charge transfer, D_3^+ , SiH_4 , fluorine azide, FN_3 , laser initiated decomposition, IR, UV-Vis, ultraviolet, visible, spectroscopy, H_3O , N_2O_2 , dinitrogen dioxide, CO, carbon monoxide, CH, high spin states, spin forbidden, radiative transition, electronic structure, molecular geometry, rare gas fluorides, NF_5 , nitrogen pentafluoride, high oxidation state, rhombic structure, tetraatomics, Si_2C_2 , disilicon dicarbide, zintl, photoexcitation, metastable metals, atomic metals, metal dimers, matrix isolation, matrix, rare gas matrix, theoretical, H_3 , trihydrogen.

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A. Metropoulos and C. Nicolaides (Theoretical and Physical
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"Experimental Studies of the Properties of Trihydrogen and
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 Aron Kuppermann (California Institute of Technology)

"Theoretical Studies of the Lifetime of Metastable Trihydrogen
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"Characterization of Tetrahydrogen Via State-Selected Excitation
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William J. Marinelli, Donald S. Kaufman (Physical Sciences Inc.)

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Byron H. Lengsfeld, George F. Adams, Cary F. Chabalowski, James
 O. Jensen (Ballistic Research Laboratory), David R. Yarkony
 (Johns Hopkins Univ)

"The Influence of Condensed Phase on Metastability"
P. K. Svaminathan, C. S. Murphy, B. C. Garrett, M. J. Redmon
 (Chemical Dynamics Corporation)

"Optimized Trial Functions for Quantum Monte Carlo Study of
 H_4^+ "



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Takeshi Oka (Univ of Chicago)

New projects overview

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Lauderdale (AF Astronautics Laboratory)

"Measurement of Charge Transfer Between D_3^+ and SiH_4^+ "
A. Garscadden, P. D. Haaland (AF Aeropropulsion Laboratory)

"Explosive Decomposition of Fluorine Azide Films"
D. J. Benard (Rockwell Science Center)

"Electronic Structure and Stability of Energetic Chemical
Species"
H. H. Michels, J. A. Montgomery (United Technologies Research
Center)

"Metastable Molecular Fuels: Theoretical Study of Ion-Pair
States -- Low Lying Surfaces of H_3O^+ "
Roberta P. Saxon, Dahbia Talbi (SRI International)

"Ab Initio Calculations On High Spin States of CO and CH"
Daniel D. Konowalow (SUNY-Binghamton)

"Theoretical Studies of Spin-Forbidden Radiative Processes
and Electronically Nonadiabatic Processes Using ab initio
Electronic Structure Methods"
James O. Jensen, Byron H. Lengsfeld (Ballistic Research
Laboratory), David R. Yarkony (Johns Hopkins Univ)

"Experimental Studies on the Synthesis of New Noble Gas
Fluorides and High Oxidation State Energetic Fluorine Compounds

Involving Unusual Bonding Situations"

W. W. Wilson, K. O. Christe (Rocketdyne)

"The Prevalence of Rhombic Structures in A_2B_2 Tetraatomics"

O. F. Guner, K. Lammertsma (Univ of Alabama, Birmingham)

"Photoexcitation of Triatomic Hydrogen"

H. Helm, L. J. Lembo (SRI International)

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EXECUTIVE SUMMARY

The need for propellants capable of delivering Isp's of 600 seconds or better has led to an investigation into high energy density molecules. Such species may derive their energy from electronic excitation and metastability, unusual bonding situations, or from high energy ground states. The Air Force is currently sponsoring research in this area through the AF Astronautics Laboratory, the AF Office of Scientific Research, and the AF Aero Propulsion Laboratory. A Technical Panel*, funded by AFOSR, administered by Dr Joseph Early of Georgetown University and chaired by Dr William Stwalley from the University of Iowa provided guidance in proposal selection and insight in the form of peer review to the Air Force Steering Group. The work involves both theoretical and experimental investigations and some of the nations leading research teams. In order to derive synergistic benefits from the two types of research, the first annual High Energy Density Matter Contractors Conference was held in May 1987.

Technical issues facing the researchers include formation mechanisms, the amount of energy stored vs the molecular weight of the reaction products, duration of the energy storage (lifetime), methods of stabilization and storage, novel bonding structures, and decay mechanisms. The work can be loosely grouped under the following categories: screening; bonding and reaction studies; theory verification and specie characterization; and feasibility/stability demonstration. Theorists are performing quantum mechanical calculations to determine energy states and predict possible decomposition pathways. Experiments are underway to verify theory, characterize species, and investigate stability. Several of the important conclusions presented at this meeting are reported here.

An energetic stable state of H₄ had been predicted by Nicolaides in his maximum ionicity excited states (MIES) theory. Initial studies showed that an energy minimum existed in the ground state and first excited state of the proposed molecule. After extensive investigation, the ground state of tetrahydrogen (H₄) was found to be an unbound saddle point. This was confirmed independently by the groups from UC Berkeley (Lester), United Technologies Research Center (Michels), and the US Army Ballistic Research Laboratory (Lengsfeld). Two other MIES candidates, HLi₃ and the excited state of H₄, still show promise of stability and high energy content.

Several groups reported on powerful new computational methods developed to investigate energy configurations. Their almost simultaneous independent findings on H₄ lend great credence to the concept of "theoretical experiments" being done on supercomputers. The new computational tools allow investigators to quickly and

accurately predict the potential stability of a candidate system before it is prepared in the laboratory. Once a stable state is identified, formation and decomposition pathways can also be calculated. This greatly reduces the time and risk involved with laboratory experiments on the species.

Michels reported calculations on a new energetic oxidizer predicted to be stable in the ground state. This compound, asymmetric dinitrogen dioxide (α -N₂O₂), is an analogue of fluorine azide (FN₃) and is predicted to be a cryogenic solid.

Benard reported that FN₃ can be viewed as a loosely bound complex of N₂ and the metastable excited singlet NF. He found that by using FN₃ as a starting material, one can generate high concentrations of the excited singlet NF, a short wavelength laser species.

Yarkony presented a recently developed algorithm for treating spin interactions in the computation of radiative lifetimes. This method enables previously untenable calculations to be performed which help predict the lifetimes of candidate species.

Helm reported on a newly developed technique for experimentally observing high Rydberg states. This rather elegant method is used to precisely characterize the energy surfaces of candidate molecules.

These items represent some of the positive results gained in the first year of work by the initial HEDM investigators. There are now over twice as many efforts underway, expanding our view into new theoretical and experimental approaches. While our main objective is to identify and develop new high energy density molecules, it is important to note that we are also advancing the state of the art in chemistry and chemical physics.

*The Steering Group has established a Technical Panel to consult on the scientific merit of proposals and to provide peer group review of technical progress as research investigations proceed. Dr William Stwalley, University of Iowa, a noted specialist in both chemistry and physics chairs the Panel. Other Panel members are:

Dr Charles F. Bender	Advanced Computational Methods Center, Athens, GA
Dr William Happer	Princeton University
Dr M. Frederick Hawthorne	UCLA
Dr Ron R. Herm	Aerospace Corporation, Los Angeles, CA
Dr Marilyn Jacox	National Bureau of Standards
Dr Lewis H. Nosanow	National Science Foundation
Dr Isaac Silvera	Harvard University

AGENDA

May 12, 1987

1300 Welcome

Dr John O. Dimmock (AF Office of Scientific Research)

1310 "HEDM Research at the Air Force Astronautics Laboratory"

Stephen Rodgers (AF Astronautics Labortory) and Nathan Presser
(Aerospace Corporation)

1325 "Towards Understanding the Stability of the $H_4^*(C_{3v})$ Cluster"

A. Metropoulos and C. Nicolaides (Theoretical and Physical
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1345 "Experimental Studies of the Properties of Trihydrogen and
Tetrahydrogen"

Aron Kuppermann (California Institute of Technology)

1405 "Theoretical Studies of the Lifetime of Metastable Trihydrogen
and Tetrahydrogen"

Aron Kuppermann (California Institute of Technology)

1425 **BREAK**

1445 "Characterization of Tetrahydrogen Via State-Selected
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William J. Marinelli, Donald S. Kaufman (Physical Sciences
Inc.)

1505 "Theoretical Studies of Metastable States of He_2 and H_4 "

Byron H. Lengsfeld, George F. Adams, Cary F. Chabalowski,
James O. Jensen (Ballistic Research Laboratory), David R.
Yarkony (Johns Hopkins Univ)

1525 "The Influence of Condensed Phase on Metastability"

P. K. Swaminathan, C. S. Murphy, B. C. Garrett, M. J. Redmon
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1545 "Optimized Trial Functions for Quantum Monte Carlo Study of H_4^{*+} "

Sheng-yu Huang, Zhiwei Sun, and William A. Lester (Lawrence Berkeley Laboratory)

1605 "Spectroscopy of Polyatomic Hydrogen Ions"

Takeshi Oka (Univ of Chicago)

1625 New projects overview

Dr Steve Rodgers, Capt Bill Sowell, Lt Walt Lauderdale (AF Astronautics Laboratory), Maj Larry Davis (AF Office of Scientific Research)

1730 Social hour

May 13, 1987

0800 "Measurement of Charge Transfer Between D_3^+ and SiH_4 "

A. Garscadden, P. D. Haaland (AF Aeropropulsion Laboratory)

0820 "Explosive Decomposition of Fluorine Azide Films"

D. J. Benard (Rockwell Science Center)

0840 "Electronic Structure and Stability of Energetic Chemical Species"

H. H. Michels, J. A. Montgomery (United Technologies Research Center)

0900 "Metastable Molecular Fuels: Theoretical Study of Ion-Pair States -- Low Lying Surfaces of H_3O^+ "

Roberta P. Saxon, Dahbia Talbi (SRI International)

0920 "Ab Initio Calculations On High Spin States of CO and CH"

Daniel D. Konowalow (SUNY-Binghamton)

0940 **BREAK**

1000 "Theoretical Studies of Spin-Forbidden Radiative Processes and
Electronically Nonadiabatic Processes Using ab initio
Electronic Structure Methods"

James O. Jensen, Byron H. Lengsfeld (Ballistic Research
Laboratory), David R. Yarkony (Johns Hopkins Univ)

1020 "Experimental Studies on the Synthesis of New Noble Gas
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1040 "The Prevalence of Rhombic Structures in A_2B_2 Tetraatomics"

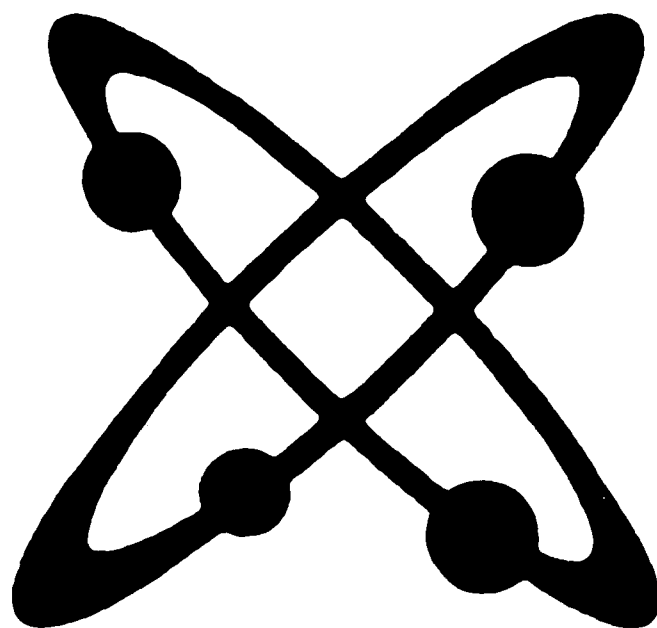
O. F. Guner, K. Lammertsma (Univ of Alabama, Birmingham)

1100 "Photoexcitation of Triatomic Hydrogen"

H. Helm, L. J. Lembo (SRI International)

1120 Concluding remarks

Dr Steve Rodgers (AF Astronautics Laboratory)



**High Energy Density Matter
Contractors Conference
1987**

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ARIES

High Energy Density Matter

Research at the

Air Force Astronautics Laboratory

HEDM IN-HOUSE RESEARCH TEAM

* Theoretical

- Two AFAL researchers
- Two on-site contract researchers
- One NRC Post-Doc

* Experimental

- One on-site contract researcher
- Two collaborative efforts with Aerospace
- Two summer professors

ARIES

HEDM Experimental Research

Facilities

- Temporary lab space
- New labs completed by Sep 87
- Equipping laboratory
Spectroscopy
Cryogenics
Flowing Afterglow

Areas of Interest

- HEDM materials in cryogenic matrices
- Rare gas compounds
- Spectroscopy

HEDM Theoretical Research

Computational Facilities

- Cray XMP
- Cray 2 (Sep 87)
- VAX 8650, 785, 750
- FPS 164/MAX
- CDC 840

Programs Implemented

- GAMESS
- Gaussian 82
- MOPAC
- MM2

Areas of Interest

- Metastable Metals
- Na.Li.B monomers, dimers, clusters
- Other HEDM candidates

High Energy Density Materials in Cryogenic Matrices

- Metal atoms, dimers, clusters
- Other candidate species
- Cryogenic liquids

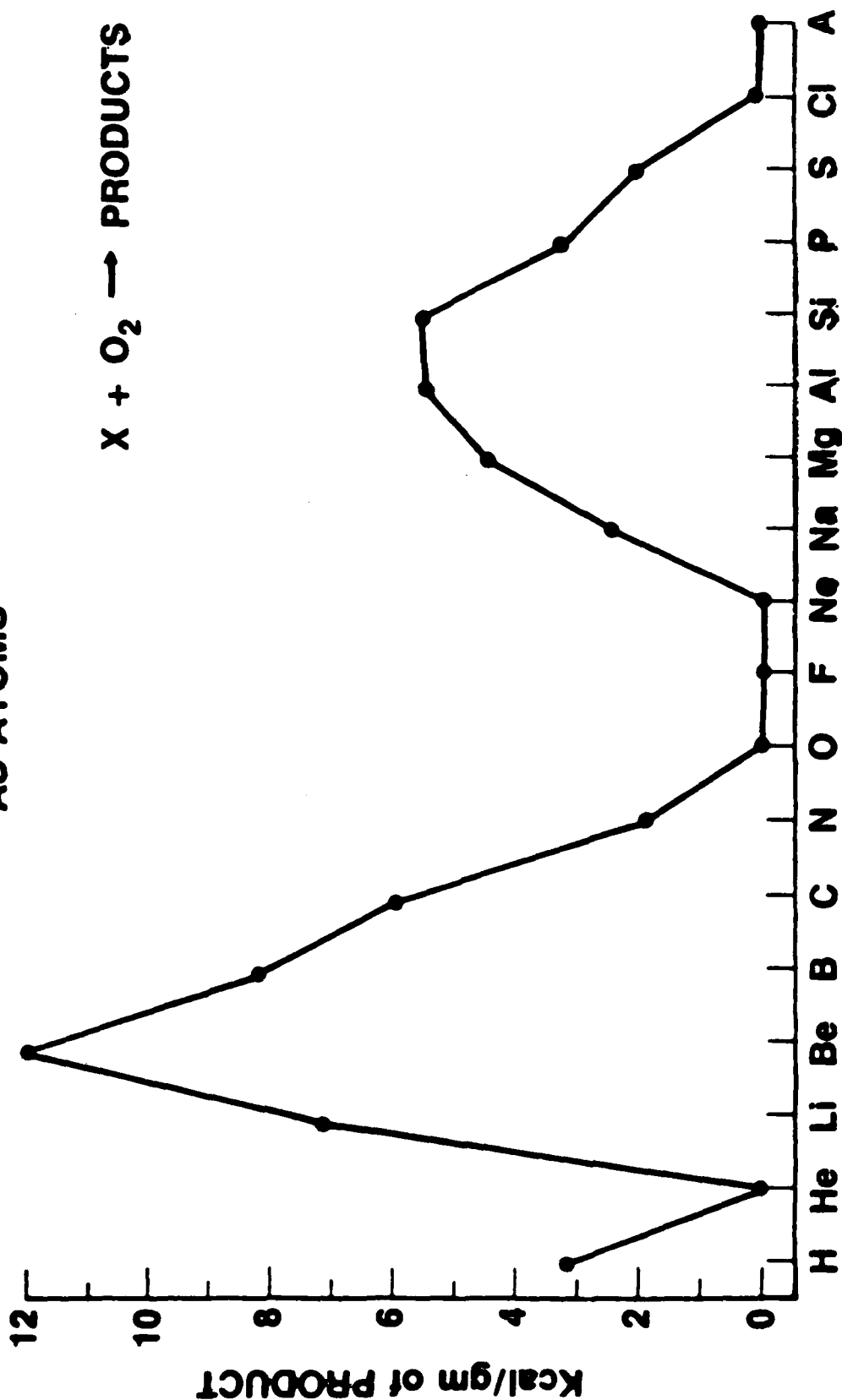
**HIGH ENERGY DENSITY MATERIALS
IN
CRYOGENIC MATRICES**

N. PRESSER and A. T. PRITT, JR.

**CHEMISTRY AND PHYSICS LABORATORY
THE AEROSPACE CORPORATION**

Combustion Energies of the Elements

AS ATOMS



Specific Impulse

- $I_{sp} = \text{THRUST/MASS FLOW}$

- $I_{sp} = V_e/g \text{ (sec)}$

V_e = MASS VELOCITY AT NOZZLE EXIT

g = GRAVITATIONAL ACCELERATION AT EARTH'S SURFACE

- $I_{sp} \propto (\text{enthalpy of reaction/product mass})^{1/2}$



Properties of Atoms in Cryogenic Matrices

- ENTHALPY OF ATOM IN MATRIX = ENTHALPY OF ATOM IN GAS
- EVIDENCE:
 - SPECTRA OF SMALL MOLECULES IN CRYOGENIC MATRICES ARE WEAKLY PERTURBED
 - VIBRATIONAL FREQUENCIES ARE ONLY VERY SLIGHTLY SHIFTED FROM GAS PHASE VALUES
 - VIBRATIONAL RELAXATION MEASUREMENTS INDICATE THAT MATRICES MAY BE TREATED AS GASES OF COMPARABLE DENSITY
 - MATRICES ARE HELD TOGETHER BY RELATIVELY WEAK DISPERSION FORCES



Specific Impulse

- $I_{sp} = \text{THRUST/MASS FLOW}$

- $I_{sp} = V_e/g \text{ (sec)}$

$V_e = \text{MASS VELOCITY AT NOZZLE EXIT}$

$g = \text{GRAVITATIONAL ACCELERATION AT EARTH'S SURFACE}$

- $I_{sp} \propto (\text{enthalpy of reaction/product mass})^{1/2}$



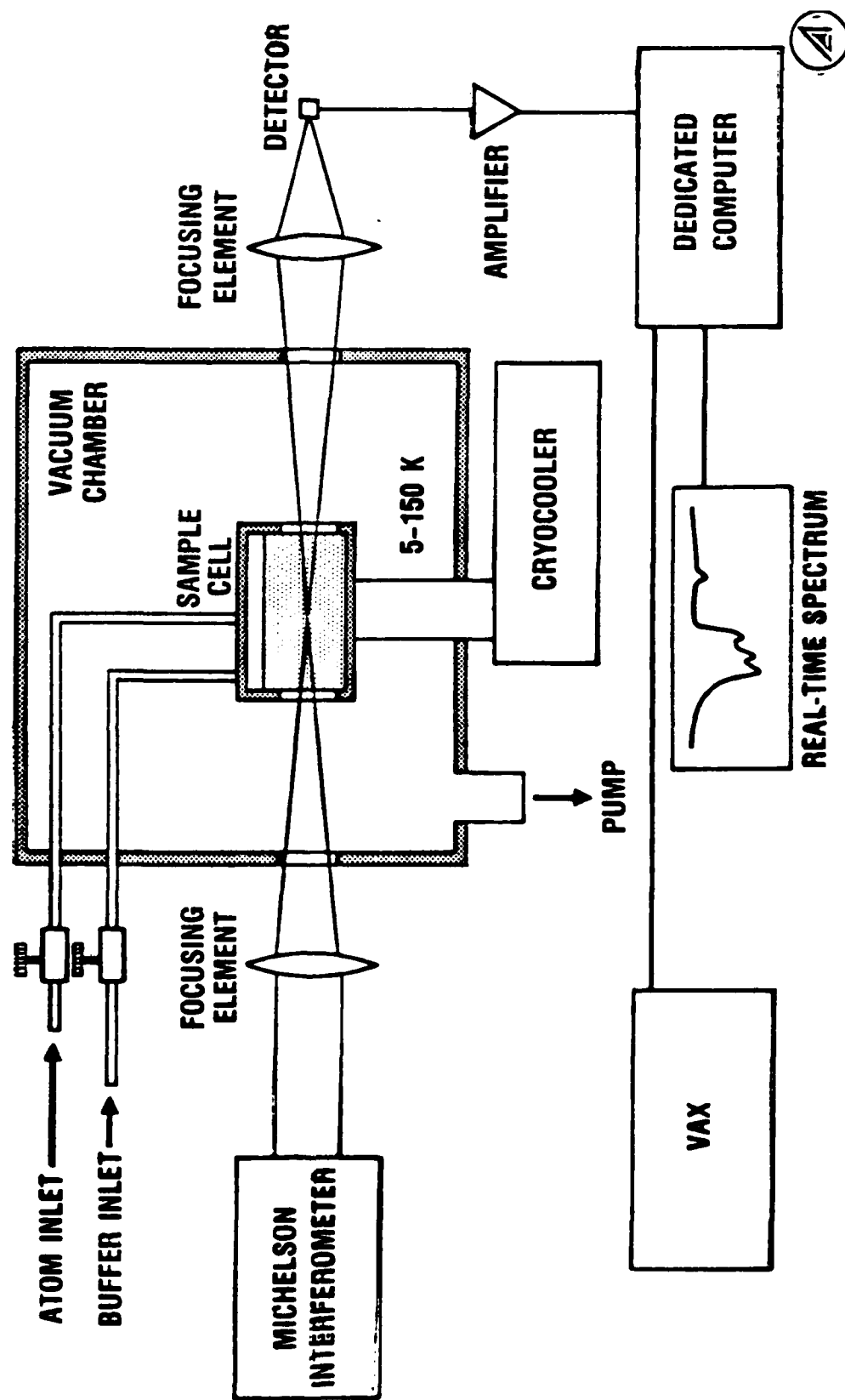
Comparison With $\text{LO}_x + \text{H}_2$ System

- FIGURE OF MERIT = ENTHALPY OF REACTION/PRODUCT MASS
- FIGURE OF MERIT FOR THE $\text{O}_2 + \text{H}_2$ REACTION IS 3.21
- BORON
 - $2 \text{ B}(\text{matrix}) + 3/2 \text{ O}_2 \rightarrow \text{B}_2\text{O}_3(\text{s}) (=8.14)$
- $\Delta H/M = 567 \cdot X_a / (M_m + (69.6 - M_m) \cdot X_a)$
 - X_a = MOLE FRACTION OF B IN THE MATRIX
 - M_m = MOLECULAR WEIGHT OF MATRIX MOLECULE
 - 69.6 = MOLECULAR WEIGHT OF B_2O_3
- MATRIX MATERIAL = H_2

X_a	0.0	0.02	0.05	0.10	0.25	0.50	1.0
$\Delta H/M$	0.0	3.38	5.37	6.47	7.50	7.93	8.14



Experimental Apparatus



Gaseous Energy Content

SPECIES	ΔH_F (Kcal/mole)	ΔH_F PER GRAM ATOM
H	52	52
H ₂	0	0
Li	38	38
Li ₂	50	25
Be	77	77
B	132	132
B ₂	194	97
C	170	170
C ₂	198	99
Al	77	77
Al ₂	108	54
Si	107	107
Si ₂	140	70

Key Scientific Issues TO BE INVESTIGATED

- WHAT ARE THE ENTHALPIES OF ATOMS IN MATRICES?
- WHAT ARE THE ACTIVATION ENERGIES OF CLUSTERING?
 - WHAT IS THEIR SIZE DEPENDENCE
 - WHAT IS THEIR TEMPERATURE DEPENDENCE?
 - WHAT IS THEIR MAGNITUDE
- WHAT ARE THE DIMERIZATION RATES?
- WHAT PART IF ANY DOES THE SPECIFIC MATRIX PLAY IN THESE PROCESSES?
- CAN THE ATOMIC SPECIES BE STABILIZED AT THE MONOMER OR DIMER LEVEL?
 - WHAT ARE THE CHARACTERISTICS OF SUCH WEAKLY BOUND COMPOUNDS



Towards Understanding the Stability of the $H_4^*(C_{3v})$ Cluster

A. Metropoulos and C.A. Nicolaides

Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation, Athens, Greece

As a first attempt to study the stability of the $H_4^*(C_{3v})$ cluster we have used the MRD-CI methods and a medium size basis set to calculate various sections of the potential energy surfaces of its ground and first excited states. We show that these correlate to the $(X^1\Sigma_g^+X^1\Sigma_g^+)$ and $(X^1\Sigma_g^+B^1\Sigma_u^+)$ states of the two H_2 constituents respectively. Finally, we report on the calculation of the diabatic matrix elements of the vibronic interaction in the region of the avoided crossing which is crucial to the stability of H_4^* .

ON THE STABILITY OF THE H_4 EXCIMER

A. Metropoulos and C.A. Nicolaides

Theoretical and Physical Chemistry Institute
National Hellenic Research Foundation
48 Vas. Constantinou Ave., Athens 11635, Greece

HISTORICAL PERSPECTIVE

In our institute there has been a long standing emphasis on the study of atomic and molecular excited states. Within the course of these studies, it was decided in 1982 to compute the low lying excited states of the $He-H_2$ ^{system} with the objective of doing dynamics on these surfaces. The idea was to do more accurate calculations than those reported in the literature /1/ and to map a wider portion of the hypersurface including the H-H stretch and a 45° section. What was expected was the construction of accurate ground and excited states van der Waals surfaces for energy transfer calculations. In the course of the investigation it became evident that for a long enough H-H distance (4.0 bohr) and a 45° angle there was a non-van der Waals minimum of about 1.52 eV with respect to $He + H_2$. The corresponding $He-H_2$ distance was about 1.5 bohr, or, else, the closest He-H distance was 1.41 bohr. In this stable geometry there is an avoided crossing between the $He+H_2(B'\Sigma_u^+)$ excited and the $He+H_2(X'\Sigma_g^-)$ ground states as the H-H distance varies /2/ (not

present in col^linear or C_{2v} geometries). Figure 1 shows the potentials of the ground and the first excited states near the minimum. The existence of such an avoided crossing has explained for the first time the observed fluorescence quenching of HD /3/ very satisfactorily. The discovery of a geometry for HeH_2 with a chemical minimum gave rise to the so called maximum ionicity excited state (MIES) theory as a means of explaining the existence of such a minimum in terms of general chemical features. The impetus for such a theory was the fact that the $H_2(B'\Sigma_u^+)$ state is ionic at intermediate H-H distances with the maximum ionicity occurring at 4.0 bohr/4/. Thus, as He approaches H_2^* the H-H bond stretches close to the maximum ionicity limit which favors energy reduction through small overlap between $H^{\delta-}$ and He and a large Coulomb interaction between $H^{\delta+}$ and He. Support for this model comes from the fact that the equilibrium distance of the HeH^+ molecular ion is 1.44 bohr/15/ which is very close to the closest He-H distance at the equilibrium geometry.

Extending this model of bonding to larger systems of interacting singlet, closed shell moieties, one can make very useful predictions of approximate "stable" geometries of, ^{their} excited surfaces. Taking H_4^* as an example, this scheme can be described as follows. An excited state of clusters, say $(ABCD)^*$, correlating with the fragments $(AB)+(CD)^*$, is thought of as occurring by an interaction of the type $(ABC)^{\delta+} + D^{\delta-}$. The geometry of the bound $(ABCD)^*$ complex is obtained from the geometry of $(ABC)^+$, and by placing D a distance from C at which

ionic VB structures have a maximum contribution to the wave function of the $(CD)^*$ fragment. For H_4^* , the geometry of the positive ion, H_3^+ , is an equilateral triangle with side of 1.65 bohr /5/. The fourth H atom is then placed above the centre of the triangle at a distance of about 4.0 Bohr, which is the maximum ioncity distance of the $B'\Sigma_u^+$ state of H_2 /4/. Figure 2 shows the relevant geometry and the coordinate system used. The MIES prediction on H_4^* was supported by the results of MRD-CI calculations, which gave a minimum at the triangle side of 1.70 bohr and a distance of 3.8 bohr from the centre of the triangle for the fourth H /6/. The calculations were done in C_s symmetry and figure 3 shows the potentials of the two lowest A' states for various lengths of the side of the equilateral triangular base. Notice that while work on the H_4 excimer has been done by other workers for various geometries /7/, the application of the MIES scheme has lead directly to a pyramidal geometry as the minimum energy geometry for the H_4 excimer. All previous considered geometries lead only to saddle points of the H_4^* hypersurface /8/.

FURTHER INVESTIGATION OF THE H_4 EXCIMER

After the MIES theory had been succesfully tested /6/, it was decided to investigate more accurately the H_4 excimer state because we needed its character and its accurate wavefunctions and surfaces. As previously, the MRD-CI method /9/ was employed and the calculations were done in C_s symmetry, due to program

limitations, but now a larger basis set was used /10/. Our attention was focused on the following: a) Obtain more accurate surfaces and wavefunctions while maintaining the C_{3v} geometry. b) Use these wavefunctions to obtain the non-adiabatic matrix elements of the vibronic interaction in the vicinity of the avoided crossing, assuming all motions frozen except the one along R (see fig. 2). c) Verify that the first two $^1A'$ states of H_4^* correlate to the $(X^1\Sigma_g^+ X^1\Sigma_g^+)$ and $(X^1\Sigma_g^+ B^1\Sigma_u^+)$ states of two hydrogen molecules.

At this point, the approximate nature of the MIES based prediction of the geometry of the excited state minimum became evident. As it was pointed out to us /14/ and as it can be deduced from the calculations in ref. 8, if the true C_{3v} symmetry is considered, there is no avoided crossing between the first two totally symmetric states but a true crossing between an 1A_1 and an 1E state ($E = A' + A''$). The geometry of this crossing was later calculated in C_1 symmetry /12/ and it was found to be $r = 1.8$ bohr and $R = 4.225$ bohr at an energy of -2.0617 a.u. Figure 4 shows the extrapolated curves of the 1A_1 and 1E states the intersection of which has been taken as the crossing point. Obviously then, the stable geometry must be of a true C_s symmetry. From the optimization calculations with respect to motions of H_a in C_{3v} geometry, represented in figure 5, it was deduced that the C_s symmetry has to be arrived at by a deformation of the triangular base rather than by displacing H_a . We thus started searching for the optimum geometry of the triangular base.

Here, we consider only the deformation of the equilateral triangular base into an isosceles (but not into a scalene) triangle /12/. After a sequence of optimizations, we arrived at a geometry having a true avoided crossing between the X^1A' and the A^1A' states which is about 154 meV lower than the (1A_1 , 1E) crossing point (-2.0674 a.u. for the A^1A' and -2.0707 a.u. for the X^1A' (state) and which is a minimum of the A^1A' state. At this geometry, the equal sides of the isosceles triangle are 1.78 bohr each, the third side is 1.62 bohr and H_a is situated on the z axis, 3.90 bohr above the plane of the triangle. The origin of the coordinate system is taken at a point $2/3$ from the vertex of the perpendicular bisector of the isosceles triangular base. Figure 6 shows the variation of the potential with R for the optimized triangular base.

Regarding the correlations previously mentioned, table 1 shows that they are correct as stated. Although the final H_4 symmetry in this table is C_{3v} , the correlations are valid for the optimized C_s symmetry as well. This is so because in this case, the A_1 irrep of C_{3v} correlates uniquely to the A' irrep of C_s ($\sigma = \sigma_v$) /10/.

Finally, the non-adiabatic matrix elements for the radial coupling were computed in the neighborhood of the avoided crossing for the optimized $H_4^*(C_s)$ geometry. The finite differences method of Lorquet and coworkers as it has been modified for the MRD-CI programs /11/ was used. All degrees of freedom were frozen

except for the R internal coordinate. Table 2 gives the result of this calculation. Notice that while the strength of the interaction is small, it persists for a rather large interval. The usefulness of this result is that one can make an order of magnitude estimate of the transition rate to the ground dissociative state by using methods already developed for diatoms /13/.

LIFETIME OF THE H_4^* EXCIMER

A computation of the lifetime of H_4^* is very desirable. There appear to be three mechanisms by which H_4^* may dissociate: a) By a radiative transition to the ground dissociative state. The probability of this transition should be rather small due to the proximity of the levels at the avoided crossing and due to the smallness of the Frank-Condon factors away from it. b) By exciting the system to the level of the (1A_1 , 1E) crossing point. Thus, the system can be "stable" only at low vibrational states and the highest such state must be found. c) By a diabatic crossing to the ground state. The probability of this transition may very well be the factor controlling the stability of H_4^* . Calculations for the elucidation of the first two mechanisms are now in progress. Order of magnitude calculations regarding the third mechanism (for the R internal coordinate only) are contemplated for the near future.

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Table 1. Comparison between 1) the sums of the potential energies of two hydrogen molecules at infinite separation and a T shaped C_{2v} H_2-H_2 complex at large intermolecular separations (1st three columns) and 2) the potential energies of H_4^* computed with reference configurations initially corresponding to H_2-H_2 (C_{2v}) and H_4^* (C_{3v}/Cs) (last three columns). The MRDCI potential energies of the H_2 molecules are also given. For the Cs symmetries, 1A_1 should be replaced with $^1A'$; θ is the angle between H_a and the z axis. ρ is the bond length of an H_2 diatom.

Geometry	ρ (a.u.)			H_4^* (r=1.8, R=4.2 a.u.)		
	1.4	1.5	2.43	C_{2v}	Cs*	Cs+
$X \sum_g^+ X \sum_g^+$	-2.3400	-2.3375	-2.1942	-2.1418	-2.1139	-2.0619
$X \sum_{A_1}^+$	-2.3393	-2.3369	-2.1947	-2.1421	-2.1137	-2.0620
$X \sum_{g+B}^+ X \sum_u^+$	-1.8735	-1.8867	-1.8513	-1.9875	-2.0081	-2.0612
$A \sum_{A_1}^+$	-1.8730	-1.8863	-1.8506	-1.9882	-2.0080	-2.0615
$H_2 (X \sum_g^+)$	-1.16999	-1.16874	-1.09711			
$H_2 (B \sum_u^+)$	-0.70350	-0.71799	-0.75424			
* $\theta = 45 \text{ deg (Cs)}$ + $\theta = 0 \text{ deg (C}_{3v}\text{)}$						

Table 2. Non-adiabatic matrix elements (in a.u.) of the vibronic coupling along the R coordinate (R in bohr).

R	$\langle X^1 A' d/dR A^1 A' \rangle$
3.6	0.65
3.7	1.1
3.8	2.1
3.9	3.0
4.0	2.4
4.1	1.5
4.2	0.83
4.3	0.50

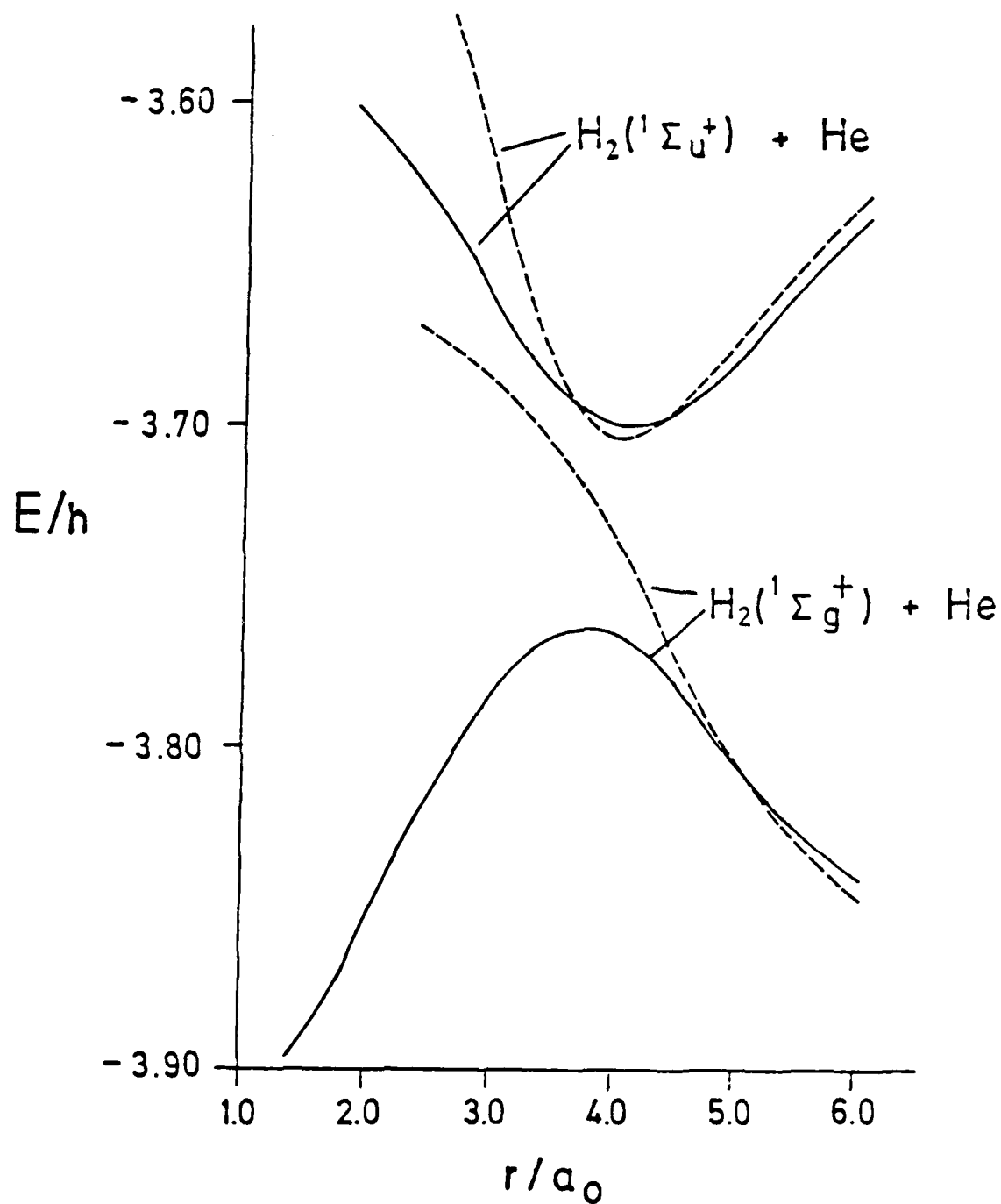


Figure 1. The potentials of the ground and the first excited state as functions of the H-H distance. — $R = 2.0$ bohr; ---- $R = 1.5$ bohr.

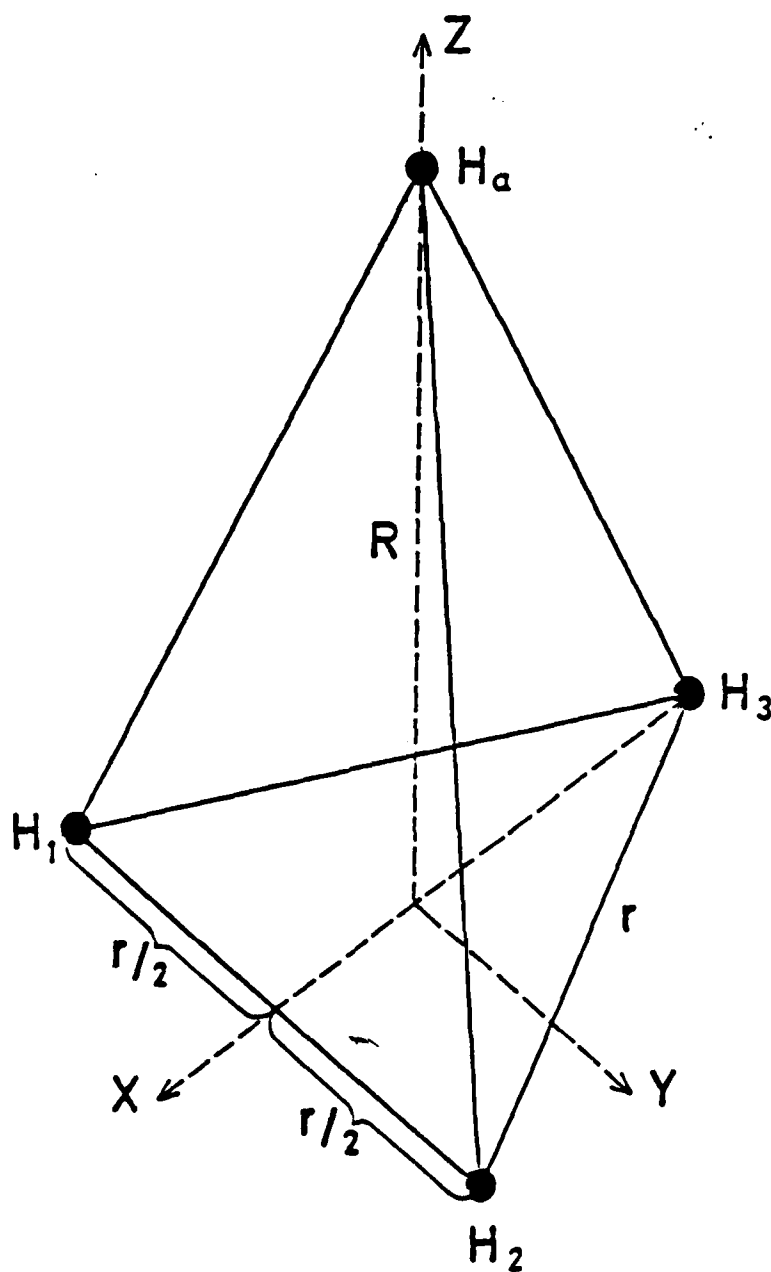


Figure 2. The coordinate system employed. The basis of the pyramid is an equilateral triangle of side r while R is the distance of the H_a atom at the apex of the pyramid from the center of the triangle. An auxiliary angle θ (not shown) may be defined on the IZ plane between the vector \vec{R} and the Z axis so that it is positive if H_a is in the first quadrant, negative if it is in the fourth quadrant and zero if it is on the Z axis ($-90^\circ \leq \theta \leq +90^\circ$).

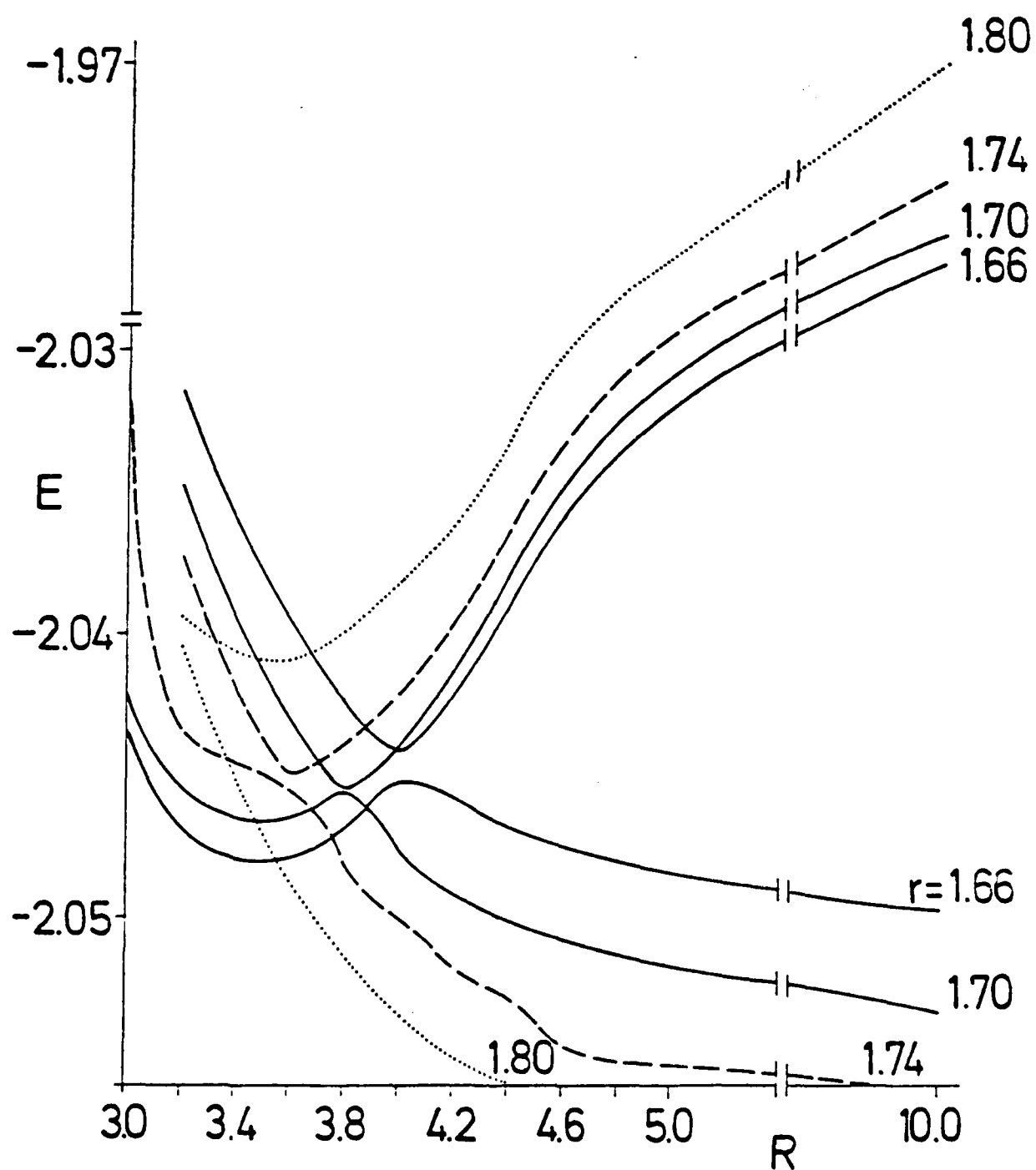


Figure 3. Potential energy surfaces (in a.u.) for the two lowest states of $1A'$ symmetry of H_4 at the trigonal pyramidal geometry shown in fig. 2.

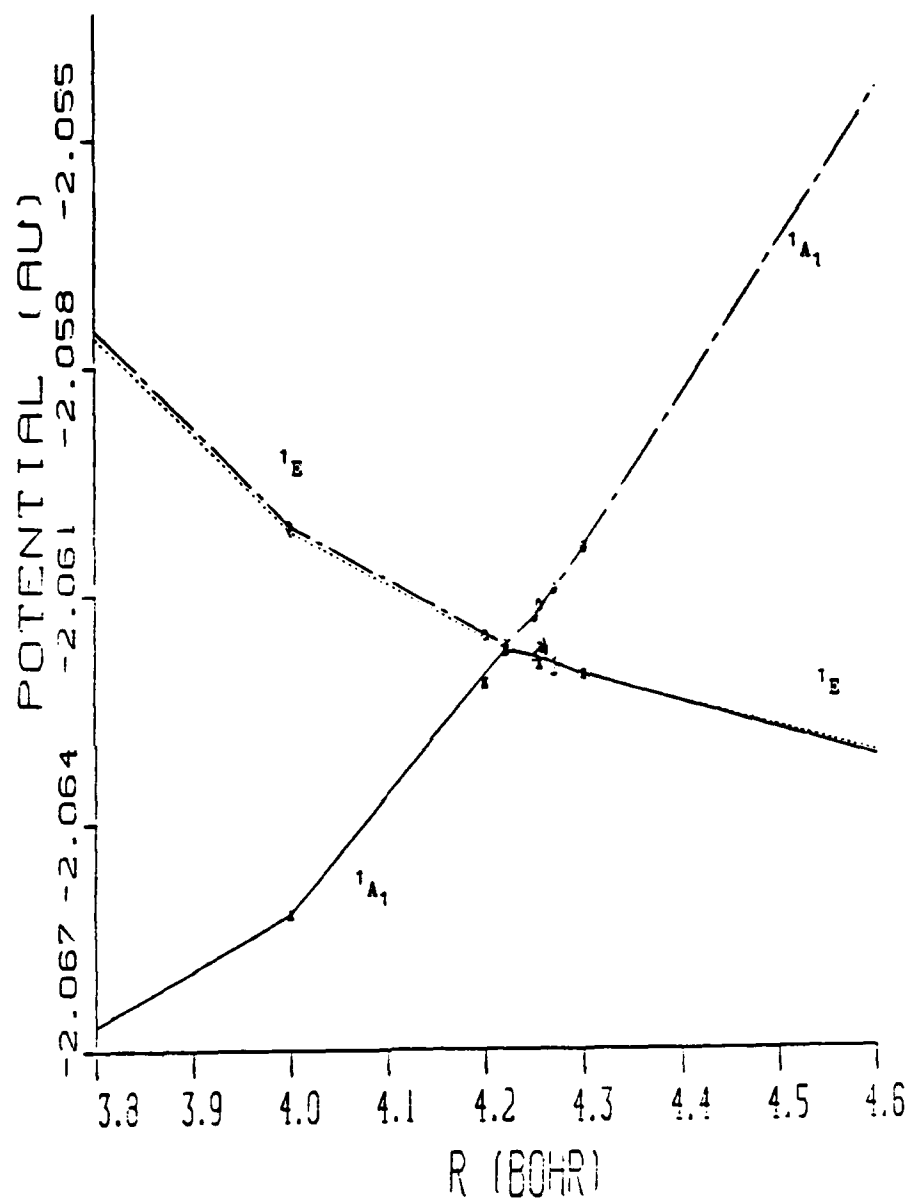


Figure 4. The crossing of the $1A_1$ and $1E$ states of H_4 (C_{3v}) appearing as an avoided crossing (done in C_1 symmetry).

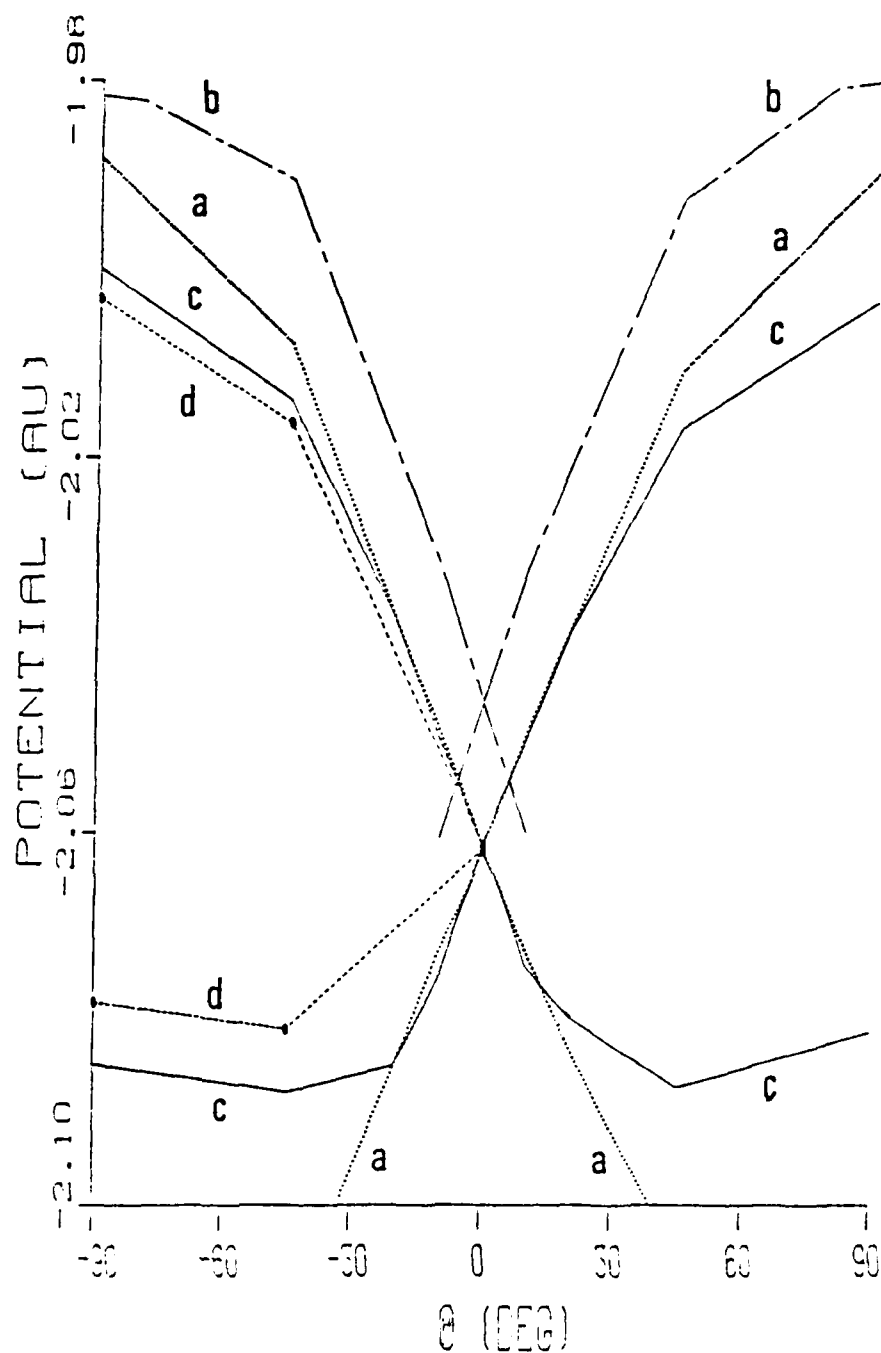


Figure 5. A section of the X^2A' and A^2A' potential energy surfaces of H_2 corresponding to a motion of H_a on the Hb plane from $\theta = -90^\circ$ to $\theta = +90^\circ$; a) Dotted line: A circular motion with $r=1.3$ and $R=1.2$ bohr b) Chained dashed line: A circular motion with $r=1.7$ and $R=1.8$ bohr from the results of ref. 6. c) Solid line: A curvilinear motion so that the energy of the A^2A' state is minimized with respect to R . d) Solid circles and connecting dashed line: A curvilinear motion so that A^2A' is minimized with respect to both r and R .

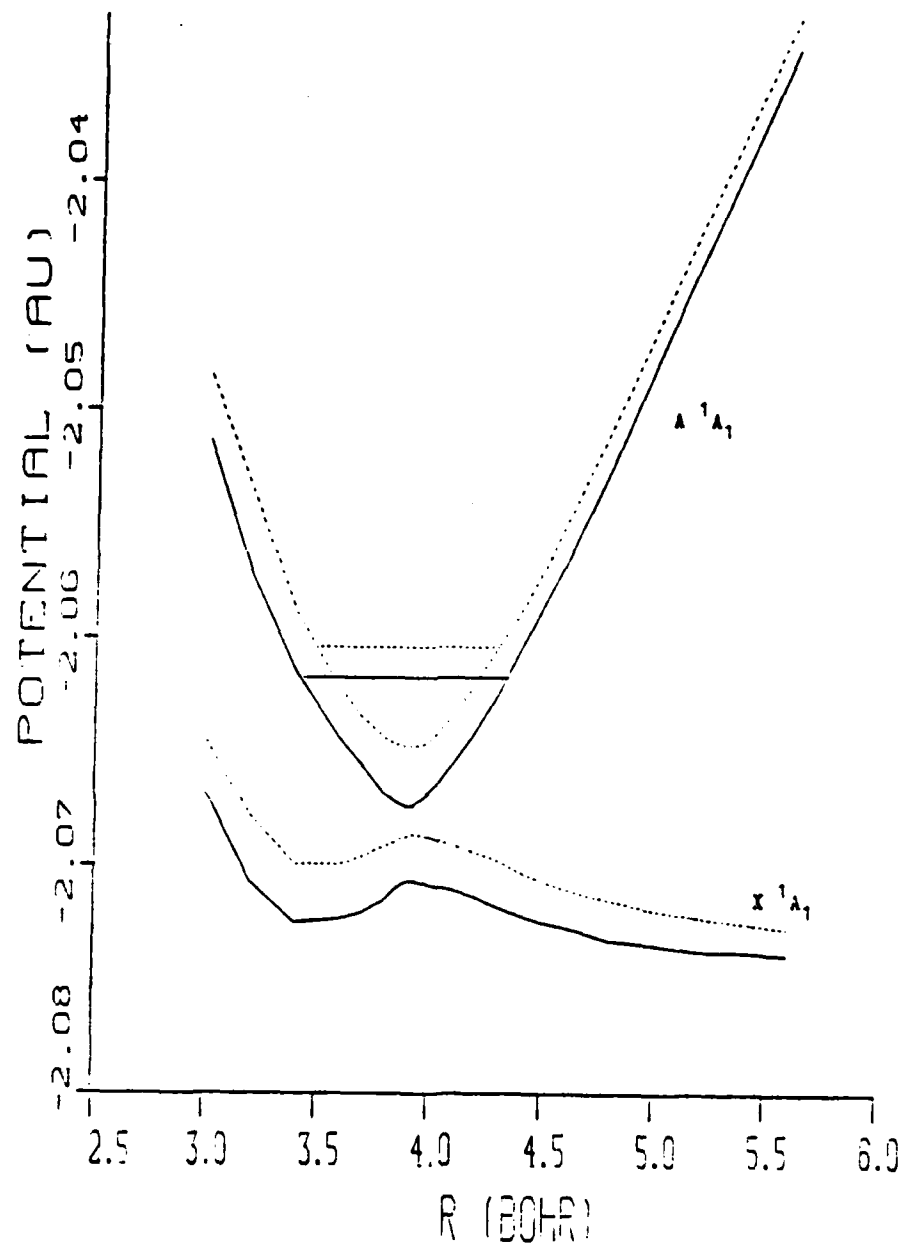


Figure 6. The variation of the potential with R for the $X\ ^1A_1$ and the $A\ ^1A_1$ states of H_4 (C_s); ---- eigenvalues; ——— extrapolated energies. The horizontal lines show the corresponding levels of the $(^1A_1, ^1E)$ crossing point.

EXPERIMENTAL STUDIES OF THE PROPERTIES OF TRIHYDROGEN AND TETRAHYDROGEN

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ABSTRACT

These studies consist in attempting to detect the existence of a metastable $1A'$ state of the H_4 molecule and in determining its lifetime. The H_4 preparation methodology consists in crossing an intense beam of metastable H_3 molecules in the $2p_z\ 2A''_2$ Rydberg state with a beam of ground state $X\ 1\Sigma^+$ HI molecules. The calculated geometry of $H_4(1A')$ is a pyramid whose base has a nuclear configuration close to that of the $2p_z\ 2A''_2\ H_3$ molecules. Furthermore, the height of that pyramid is approximately the same as the effective length of the $2p_z$ Rydberg orbital. The reaction $H_3(2p_z\ 2A''_2) + HI(X\ 1\Sigma^+) \rightarrow H_4(1A') + I(2P_{3/2})$ is endothermic by about 1 eV and the $H_3(2p_z\ 2A''_2)$ beam has an average translational energy of about 8 eV.

The crossed beam apparatus has been assembled and put into operation. The primary $H_3(2p_z\ 2A''_2)$ beam is generated in a high temperature arc discharge source through which H_2 flows. The discharge plasma emerges from a cathode nozzle orifice, and the beam passes through a skimmer, then through a differentially pumped chamber and into the main scattering chamber. The secondary beam of Ar (in control experiments) or HI (or DI) is generated by expansion of the corresponding gas through a capillary array. The scattered species are detected by a rotatable quadrupole mass spectrometer. A report will be given on the progress achieved in these experiments so far.

HIGH ENERGY DENSITY MATTER CONFERENCE

Arlington, VA.

12-13 May 1987

I. EXPERIMENTAL STUDIES OF THE PROPERTIES
OF TRIHYDROGEN AND TETRAHYDROGEN

II. THEORETICAL STUDIES OF THE LIFETIME
OF METASTABLE TRIHYDROGEN AND TETRA-
HYDROGEN

Aron Kuppermann, Caltech

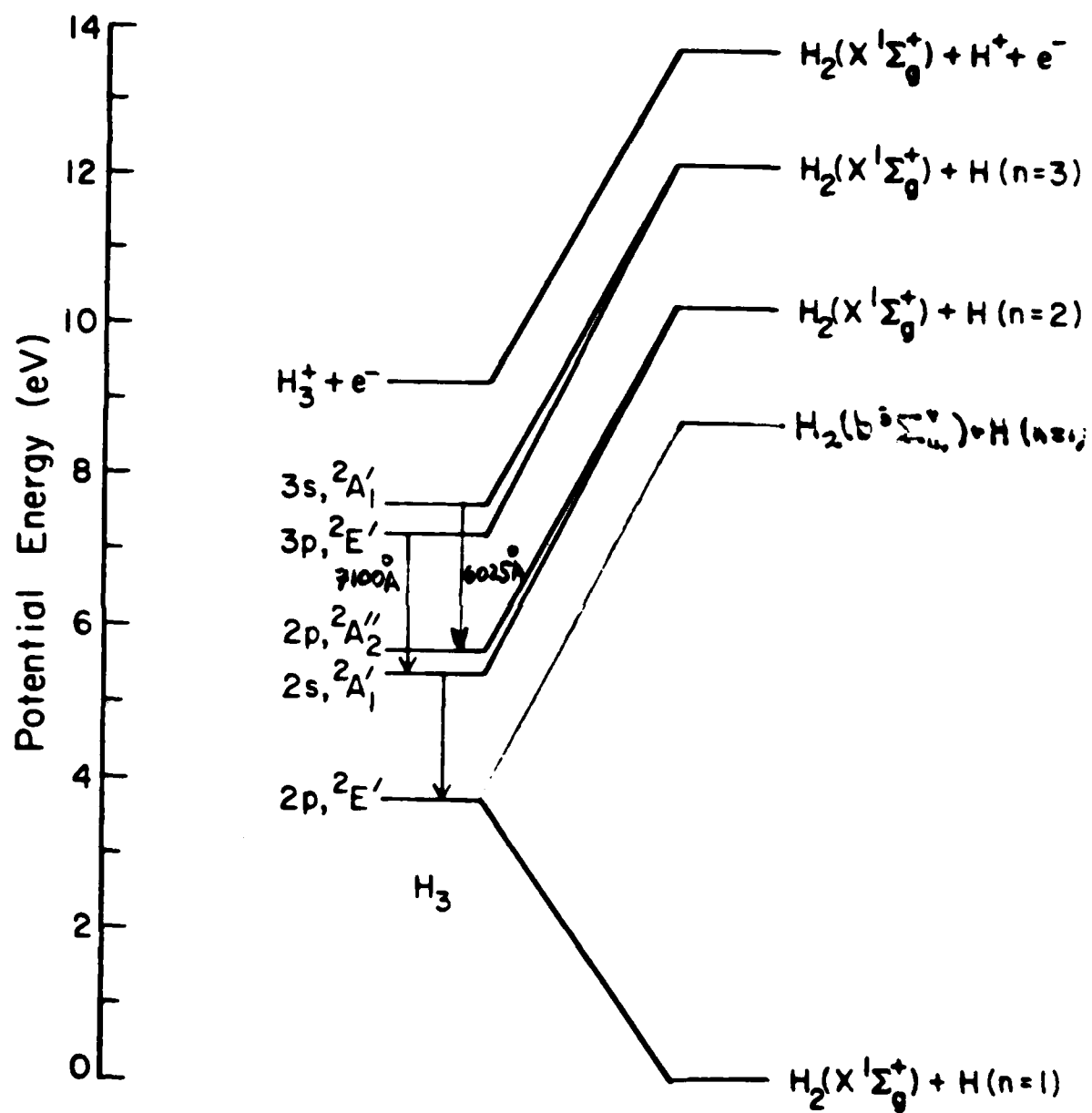
1. The spectroscopic properties of the Rydberg states of H_3 .
2. An intense beam of metastable H_3 .
3. Dynamic properties of metastable H_3 : total scattering, photoionization and surface ionization.
4. A proposed scheme for producing and detecting metastable H_4 from metastable H_3 .
5. Experiments with the crossed molecular-beam apparatus.

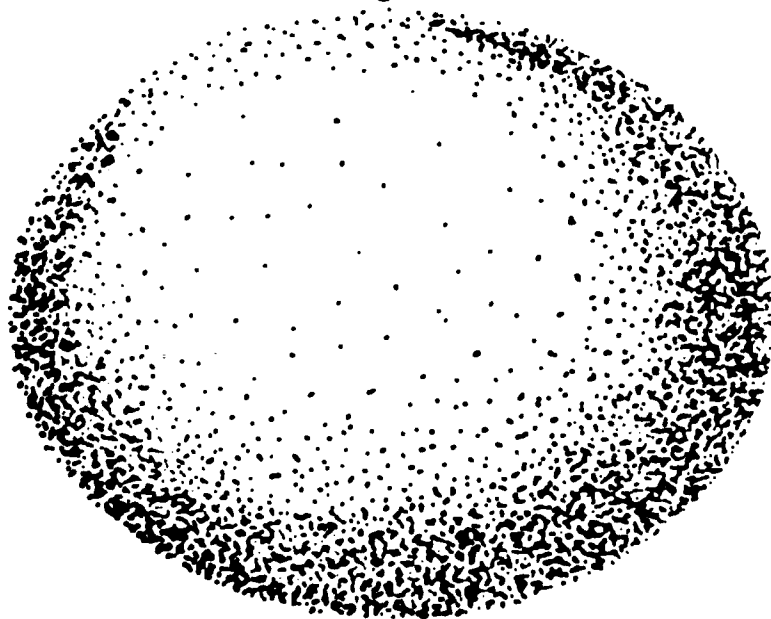
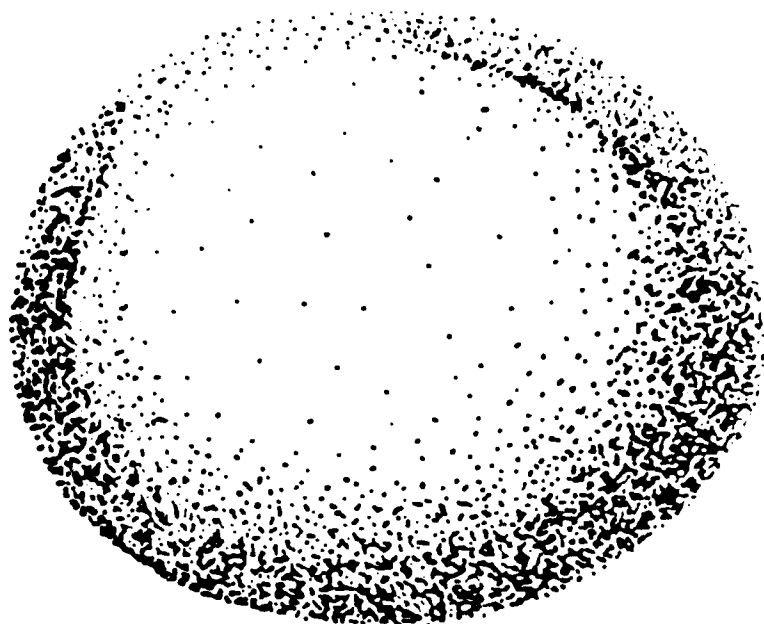
6. Radiative and predissociative selection rules for the Rydberg states of H_3 .
7. Hyperspherical coordinate calculations of the ground (continuum) state of H_3 .
8. Properties of the potential energy surface of the first excited state of H_3 (conical intersection).
9. Next steps in the experimental and theoretical efforts.

Collaborators

Experimental work: Mary Rodgers, Q. Jin and Z. Peng.

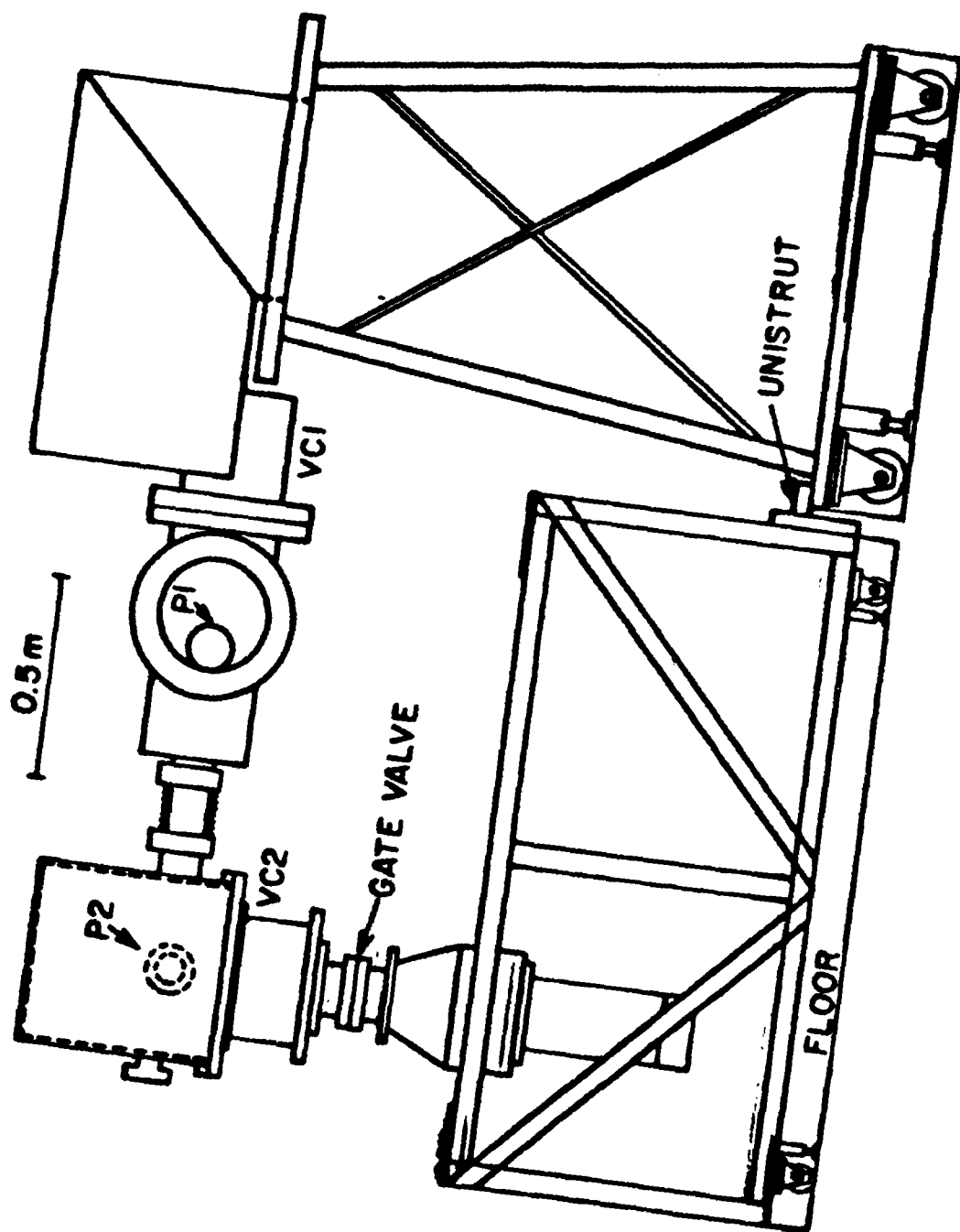
Theoretical work: Paul Hipes, Steve Cuccaro, Mark Wu and Z. Peng.

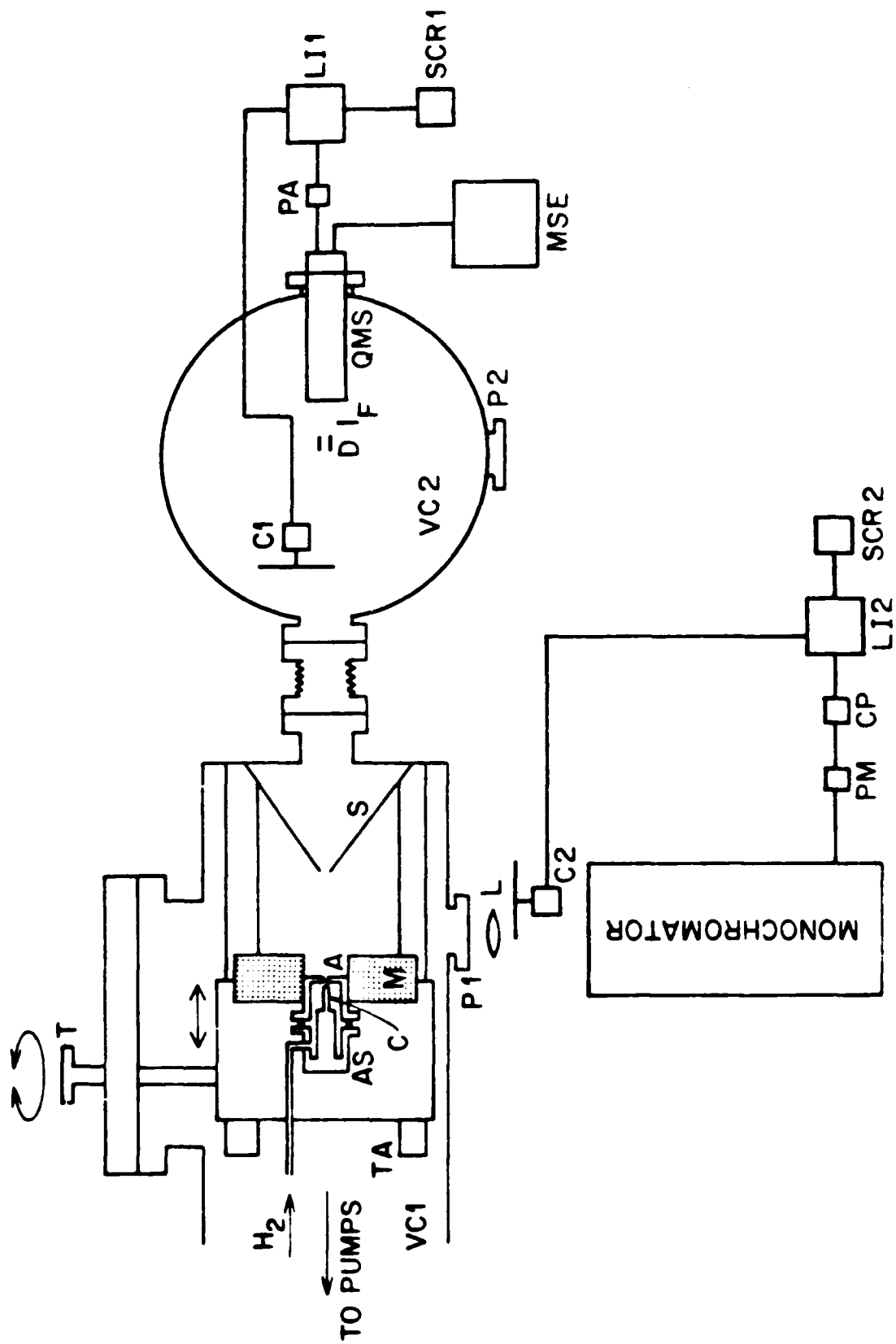


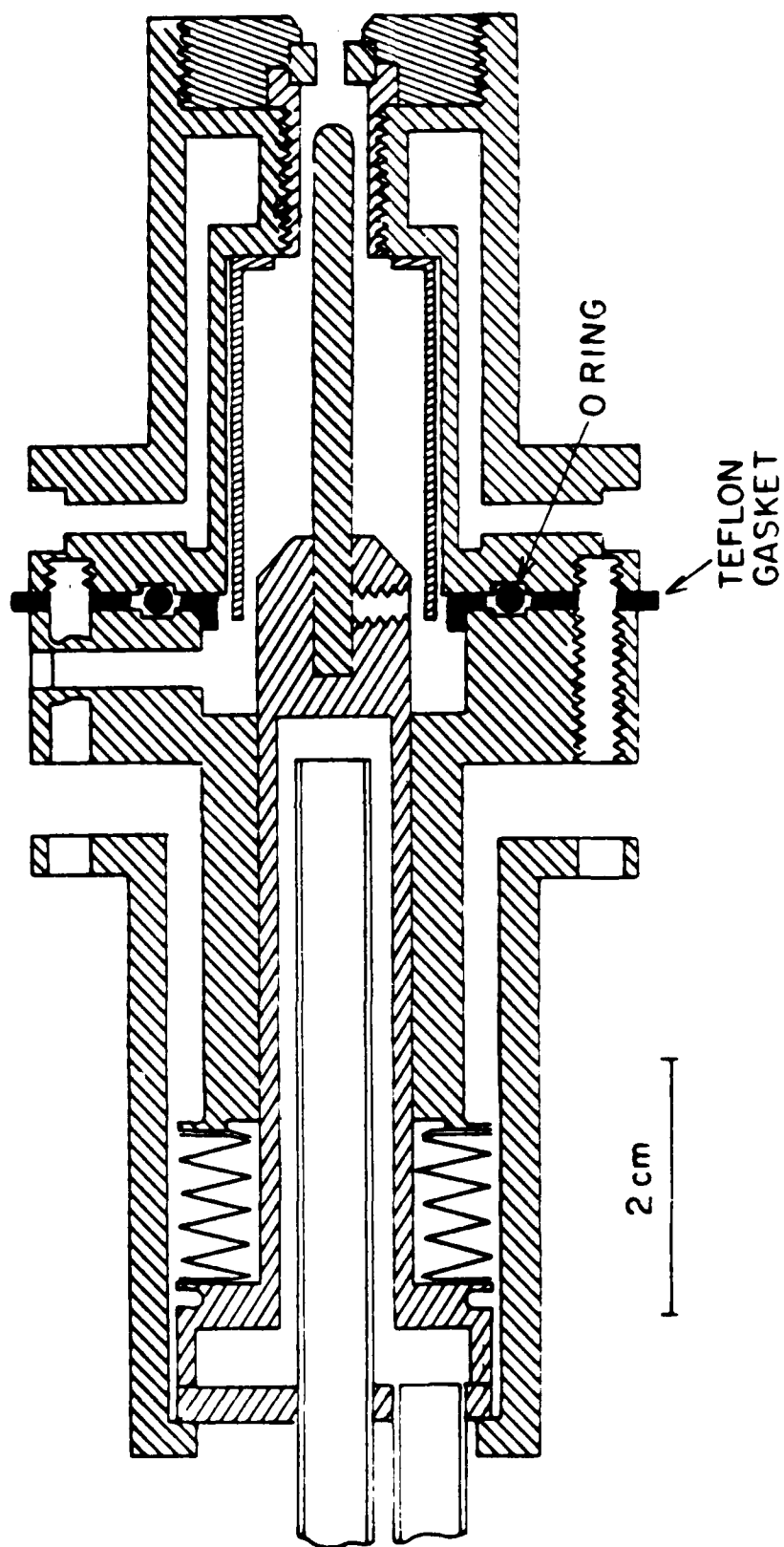


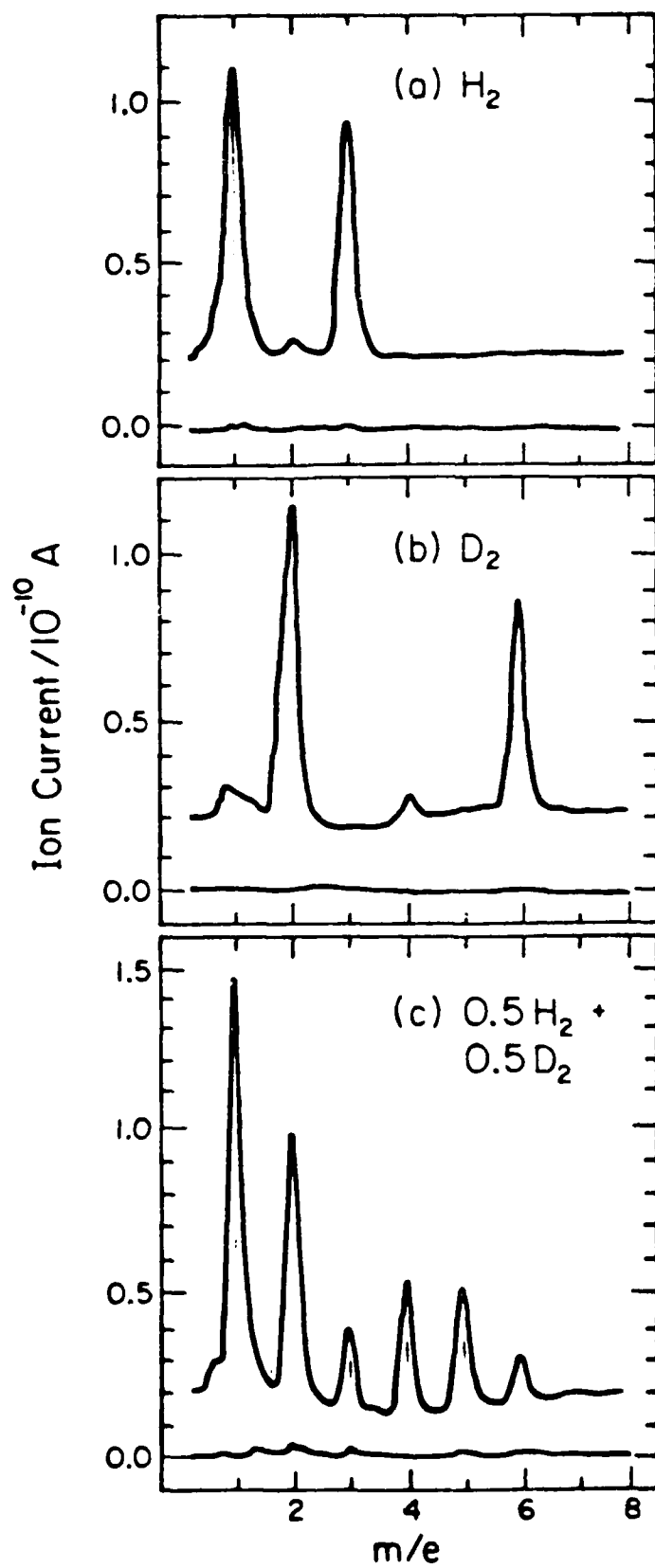
2 Å

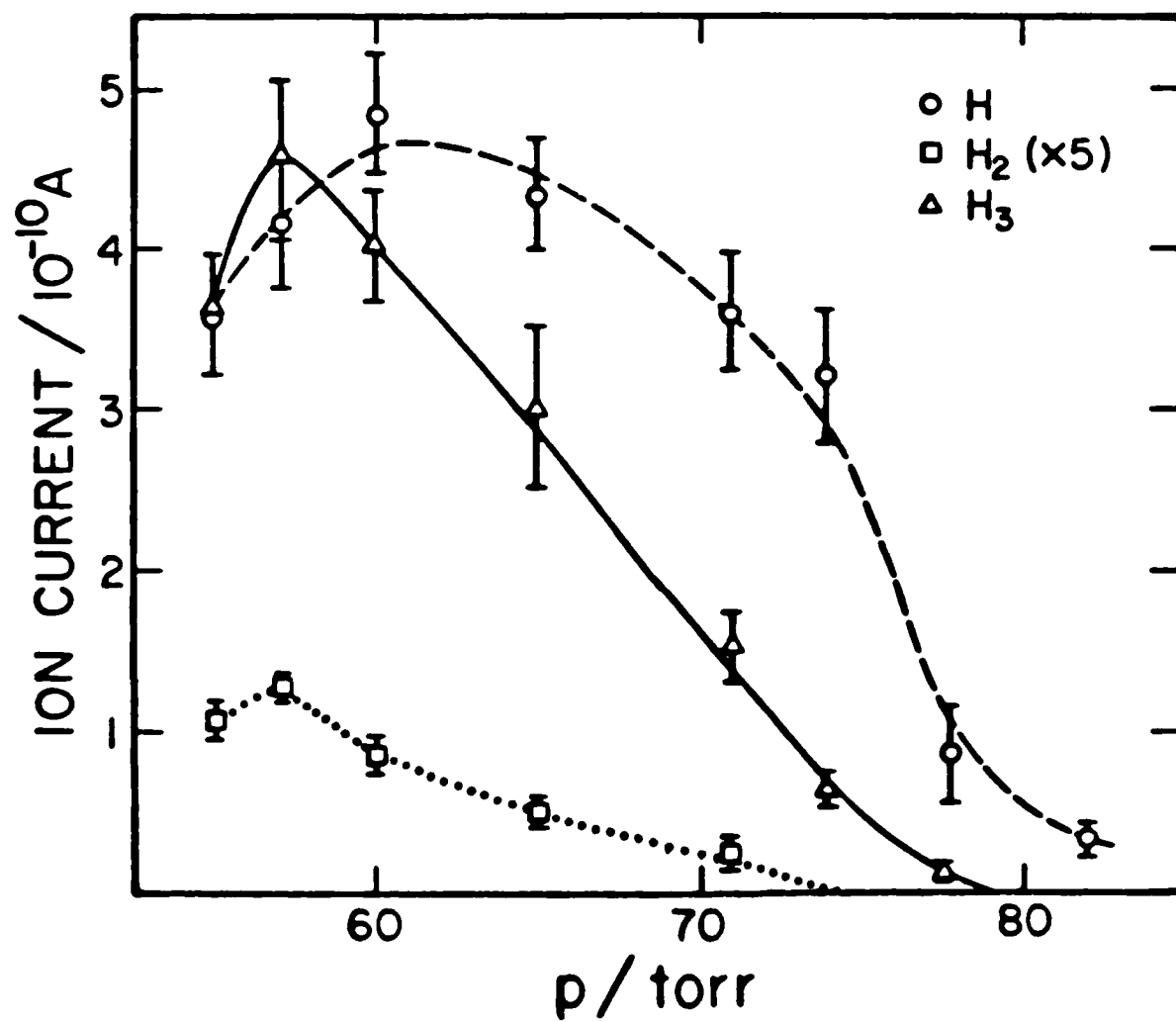
A horizontal scale bar with vertical end caps, indicating a length of 2 Å.

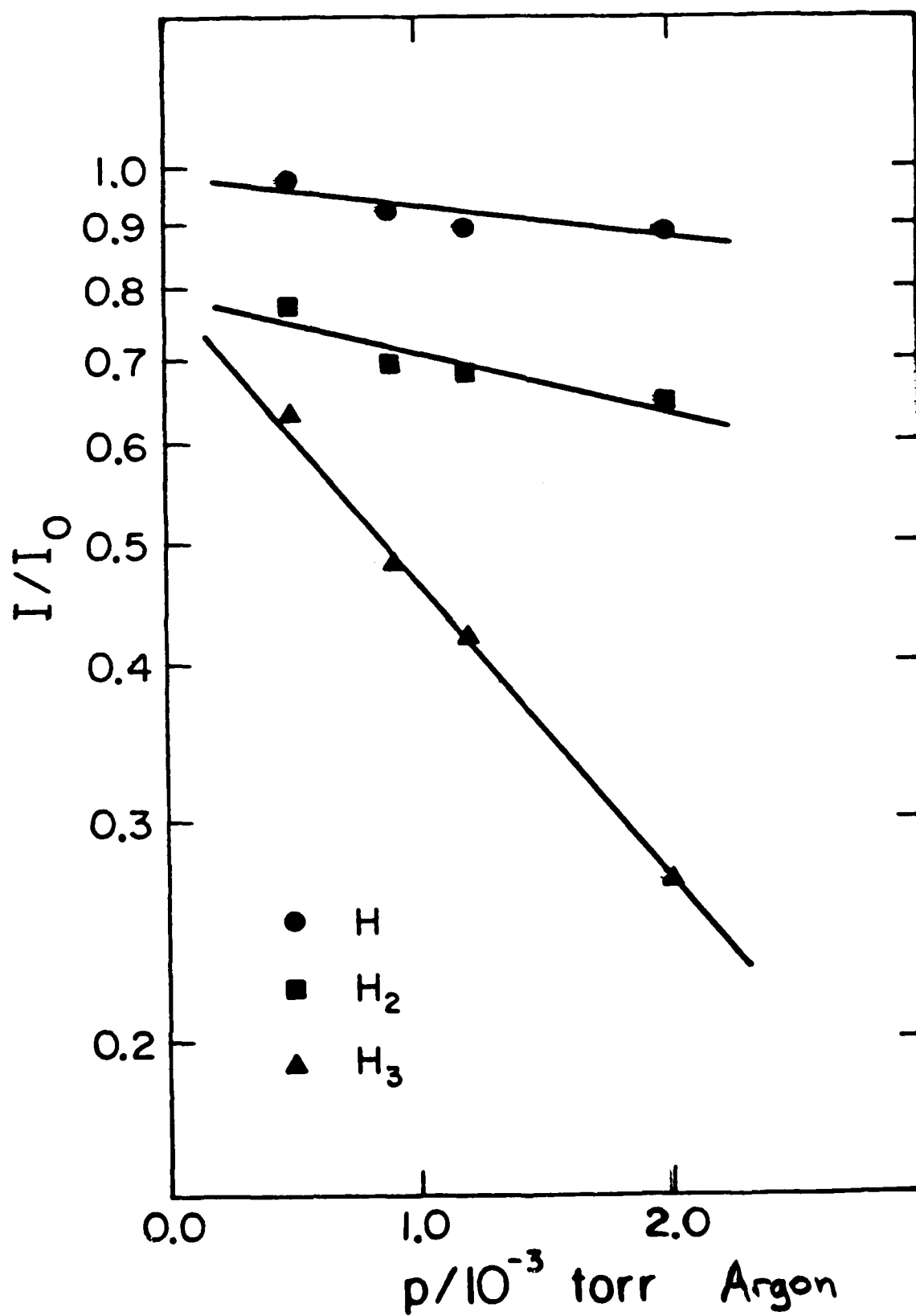


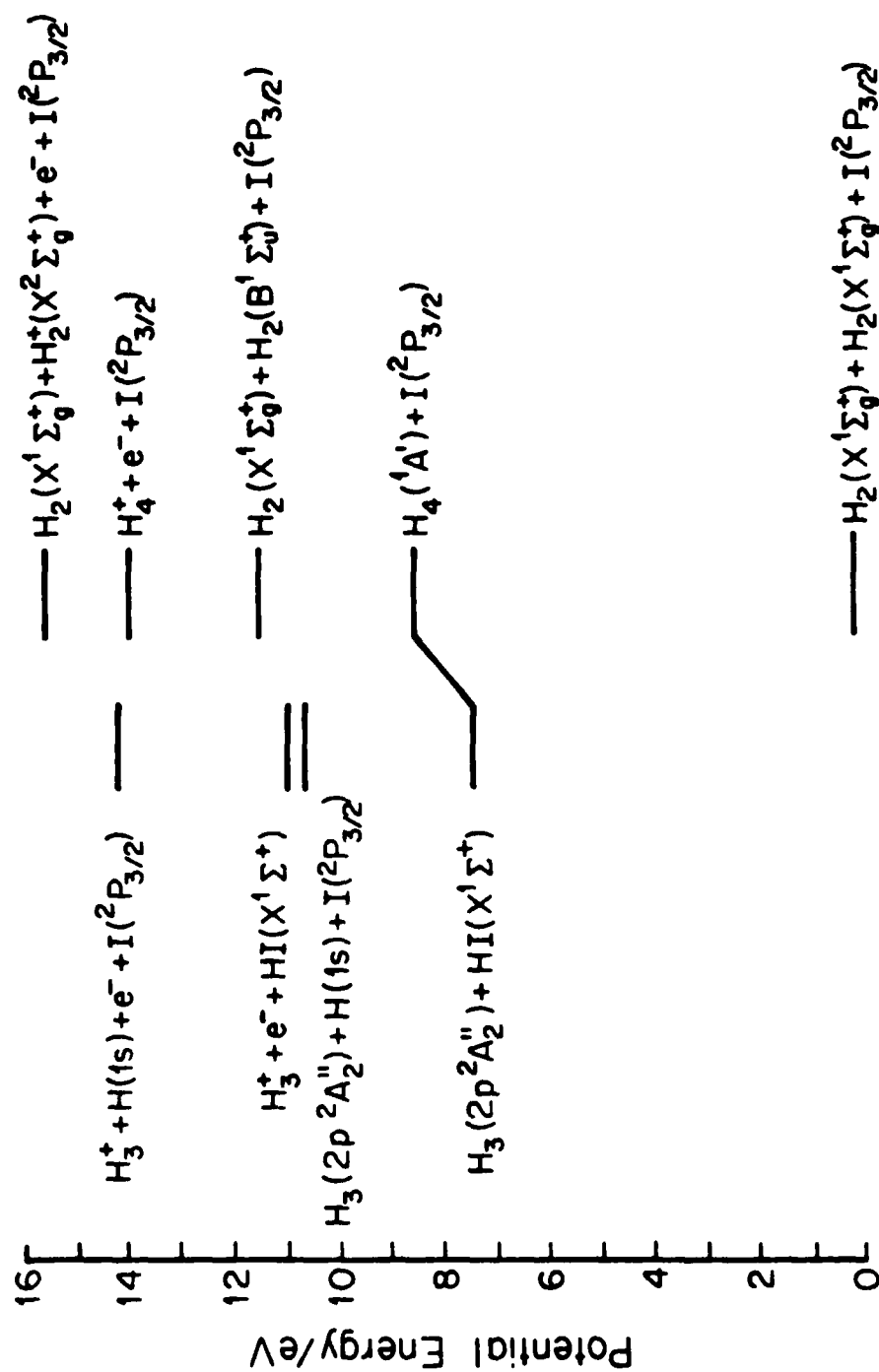


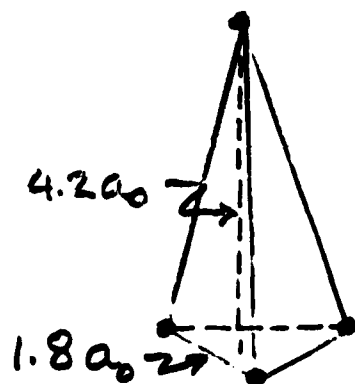






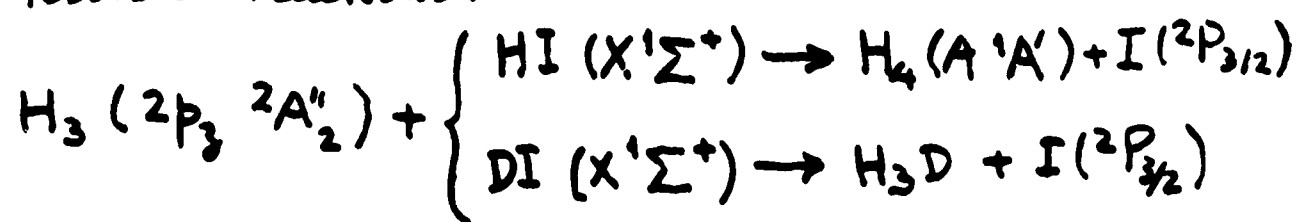


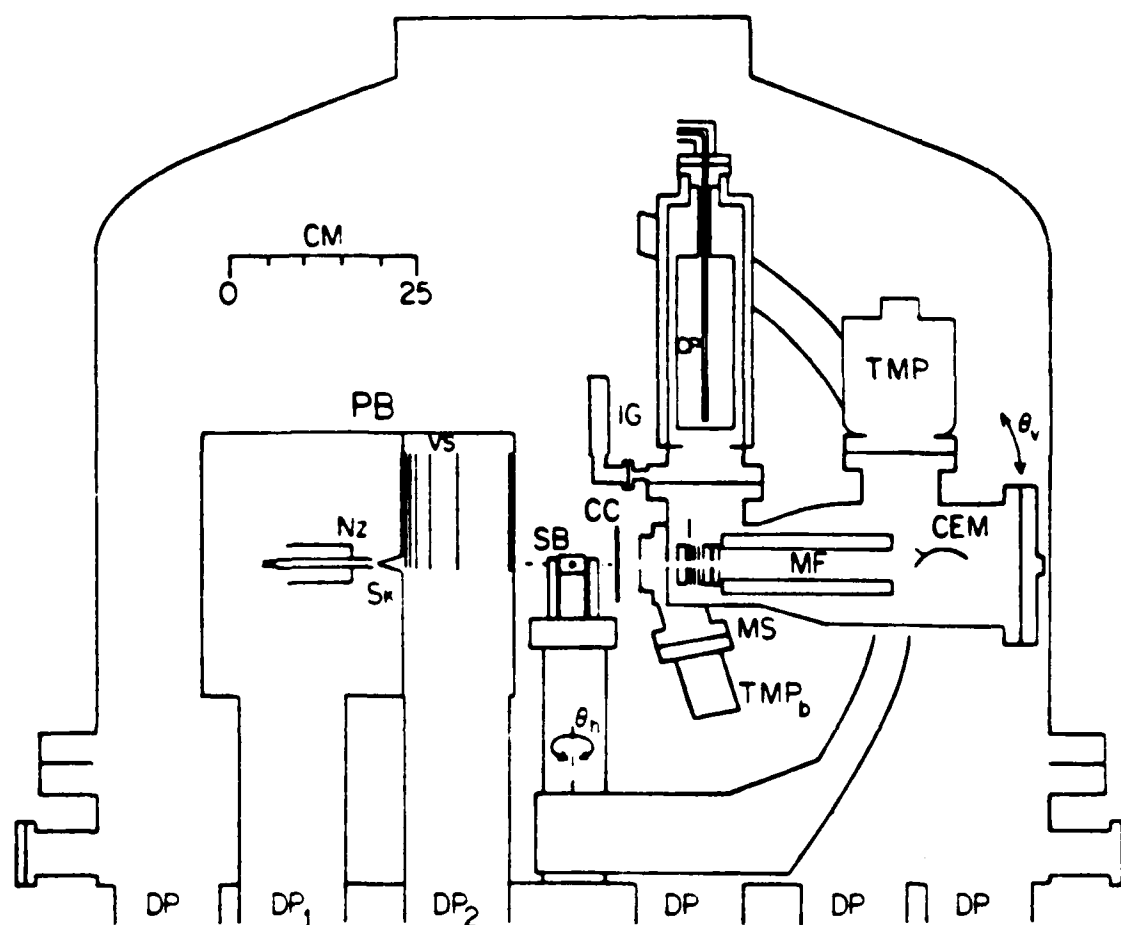




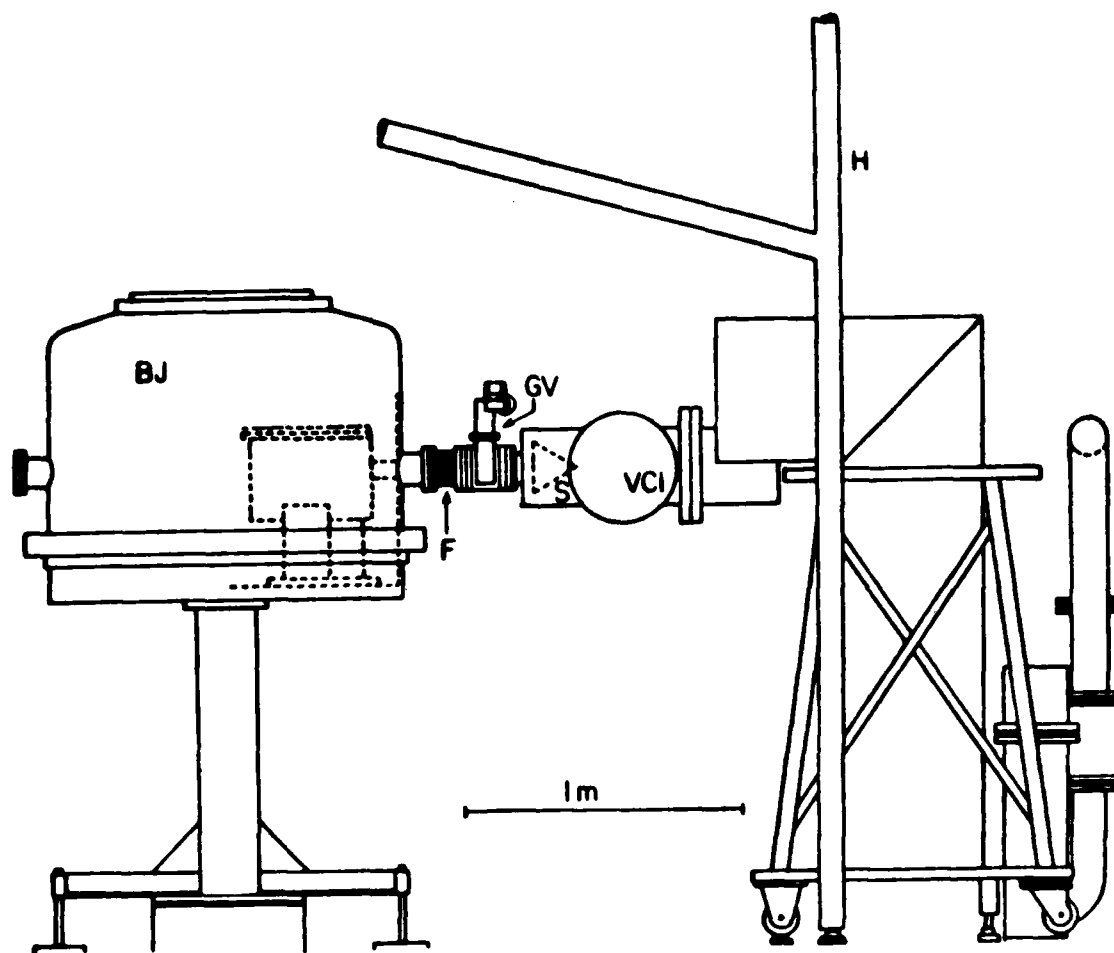
Geometry of $A' {}^1A'$

Possible reactions:





Vertical cut view of the crossed molecular beam apparatus, drawn approximately to scale. DP - diffusion pumps, PB - primary beam source (with the beam axis in the plane of the drawing), Nz - nozzle, SK - skimmer, VS - velocity selector, SB = secondary beam source (with the beam perpendicular to the plane of the drawing), CC = correlation chopper blade, MS = mass spectrometer detector, TMB_b = 50 l/s turbomolecular pump for buffer chamber, I = ionizer and ion-focus lenses, CEM = channeltron electron multiplier, CP = 350 l/s liquid He cryopump, TMP = 360 l/s turbomolecular pump, IG = ionization gauge.



Side view of hybrid apparatus with the metastable H_3 arc discharge primary beam source connected to the crossed molecular beam apparatus. VC1, vacuum chamber; S, water-cooled copper skimmer; GV, pneumatic gate valve; F, flexible flange; B5, 50-inch bell jar. Dashed lines indicate box within the bell jar which contains the magnetic velocity selector.

5. Experiments with the crossed molecular beam apparatus.

Since the last HEDM meeting (March 87), we have:

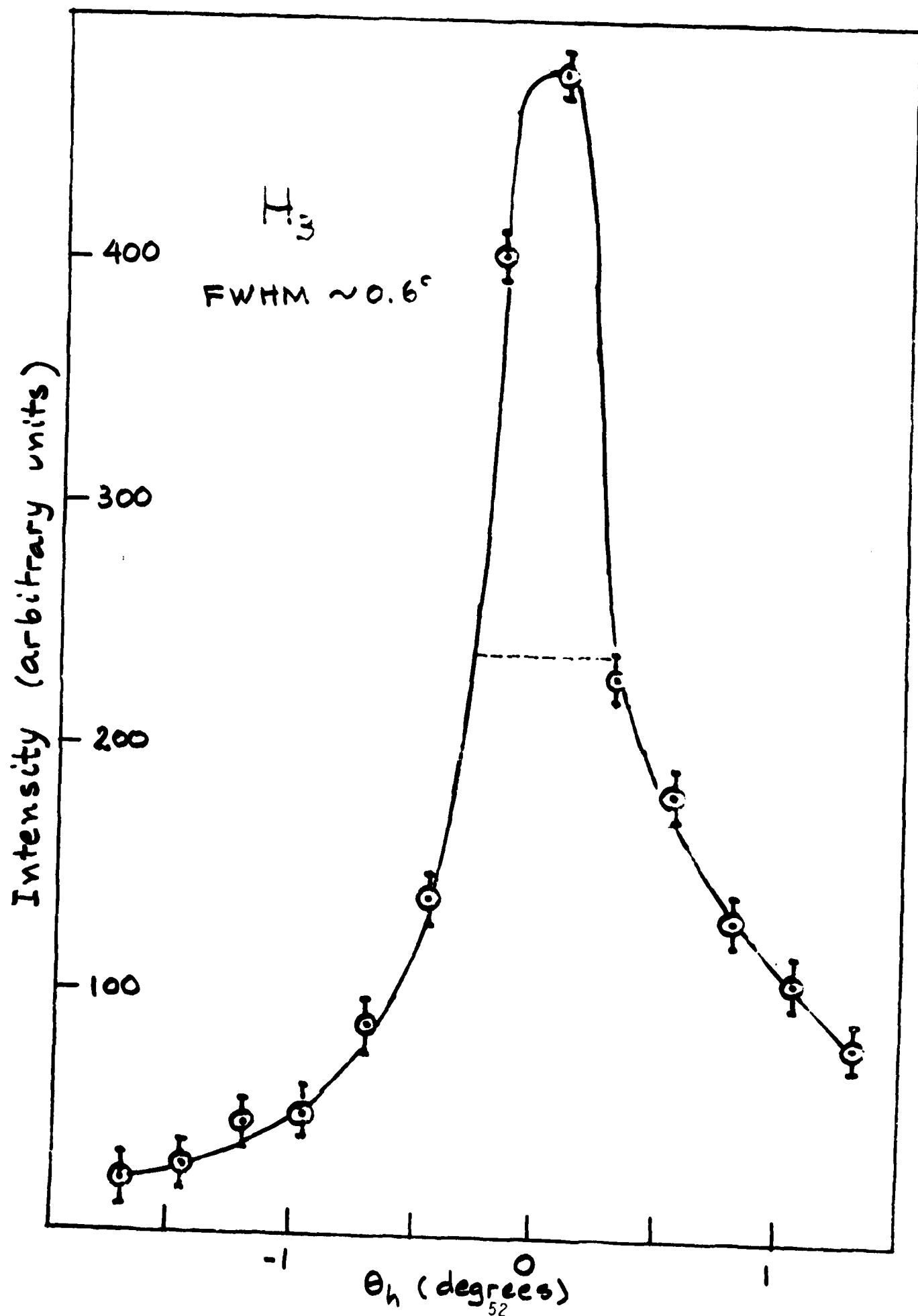
- Performed 150 runs with the H_2 beam
- Each run lasted an average of 5 hours, for a total running time of 750 hours.
- Made 3 major changes in the apparatus:
 - a. Rebuilt the arc source to eliminate the bellows and shorten the length of the cathode rod.
 - b. Built a simple beam steering mechanism.
 - c. Rebuilt the arc source electromagnet.

The objective of these changes was to overcome the following experimental difficulties:

- Interference due to the intense light emitted by the arc.
- Stringent alignment requirements ($\pm 0.05^\circ$).
- Beam position shifts during runs due to deformation of cathode

These difficulties have been overcome one by one. We are currently running the beam 4 times a week, each run lasting about 8 hours. Each anode and cathode last for an average of 6 runs.

Crossed beam experiments $H_3(2p, {}^2A''_2) + A-$ have now been started. These are preparatory experiments (of a background nature) for the $H_3(2p, {}^2A''_2) + HI, DI$ runs.



THEORETICAL STUDIES OF THE LIFETIME OF METASTABLE TRIHYDROGEN AND TETRAHYDROGEN

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ABSTRACT

The $2p_z\ 2A''_2$ Rydberg excited state of H_3 is known experimentally to be metastable, but its predissociative lifetime has neither been measured nor calculated, although a lower bound of 40 μsec has been experimentally estimated for it. Furthermore, the potential energy surface of the $1A'$ state of H_4 has been calculated to have a well whose depth is 1.86 eV. The objective of our theoretical studies is to perform calculations of the predissociative lifetimes of both of these molecules.

The initial calculations are being performed for the H_3 system. We are using initially a double many-body expansion (DMBE) of the two lowest potential energy surfaces of H_3 . The computation involves three steps: a) Scattering calculations on the lowest state. We have performed these accurately for energies up to 1.6 eV using hyperspherical coordinates and are investigating approximate methods for extending them to the higher energies required. b) Bound state calculations on the upper surface. The structure of that surface is being analyzed and a selection is being made of the basis functions to be used. c) Interaction matrix calculations. These have not yet been initiated. The results obtained so far will be presented and discussed.

Radiative and predissociative selection rules for the Rydberg states of H_3 .

1. Radiative selection rules

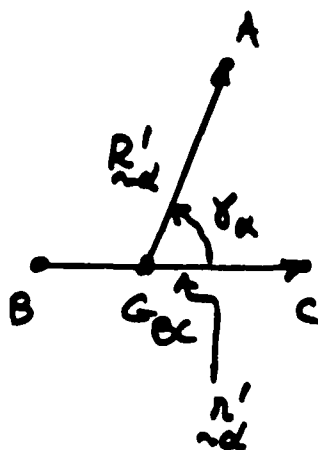
Transition	El. dipole	Mag. dipole	El. quadrupole
$2p_3 \ ^2A''_2 \rightarrow 2p_x \ ^2E'$	forbidden	allowed	allowed
$2p_3 \ ^2A''_2 \rightarrow 2s \ ^2A'_1$	allowed	forbidden	forbidden
$2s \ ^2A'_1 \rightarrow 2p_x \ ^2E'$	allowed	forbidden	allowed

2. Predissociative selection rules

Transition	Electronic	Vibronic	Rovibronic
$2p_3 \ ^2A''_2 \rightarrow 2p \ ^2E'$	forbidden	forbidden	allowed for $J \neq 0$
$2s \ ^2A'_1 \rightarrow 2p \ ^2E'$	forbidden	allowed	

To calculate transition life-times, the following quantities are needed:

- The rovibrational wave function of the upper state
- The scattering (continuum) wave function of the lower state
- The coupling operator (electromagnetic or electronically non-adiabatic predissociative) between these states



$$R_\alpha = \left(\frac{\mu_{A,BC}}{\mu} \right)^{1/2} R'_\alpha$$

$$r_\alpha = \left(\frac{\mu_{BC}}{\mu} \right)^{1/2} r'_\alpha$$

$$\mu = \left(\frac{m_A m_B m_C}{m_A + m_B + m_C} \right)^{1/2}$$

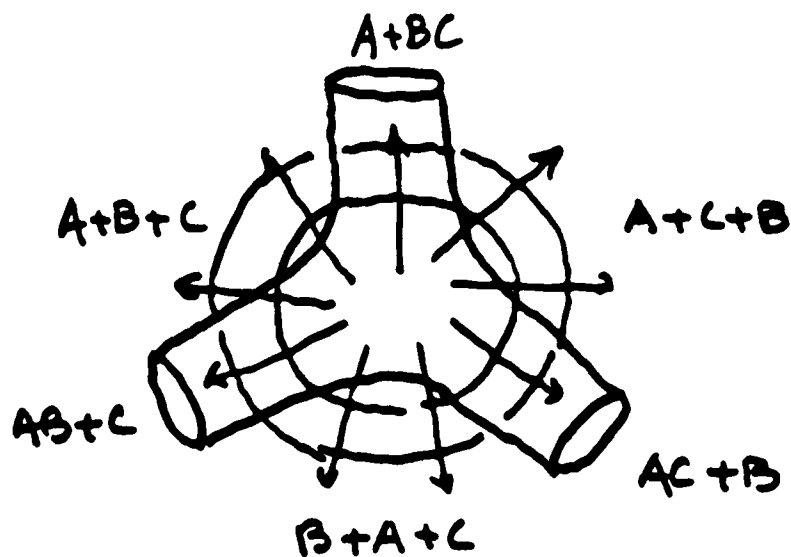
$$\rho = (R_\alpha^2 + r_\alpha^2)^{1/2}$$

$$\omega_\alpha = 2 \tan^{-1} \frac{r_\alpha}{R_\alpha}$$

$$R_\alpha, r_\alpha \Rightarrow \rho, \omega_\alpha$$

$$R_\alpha, \theta_\alpha, \phi_\alpha, r_\alpha, \gamma_\alpha, \psi_\alpha \Rightarrow \rho, \omega_\alpha, \theta_\alpha, \phi_\alpha, \gamma_\alpha, \psi_\alpha$$

$$V = V(\rho, \omega_\alpha, \gamma_\alpha)$$

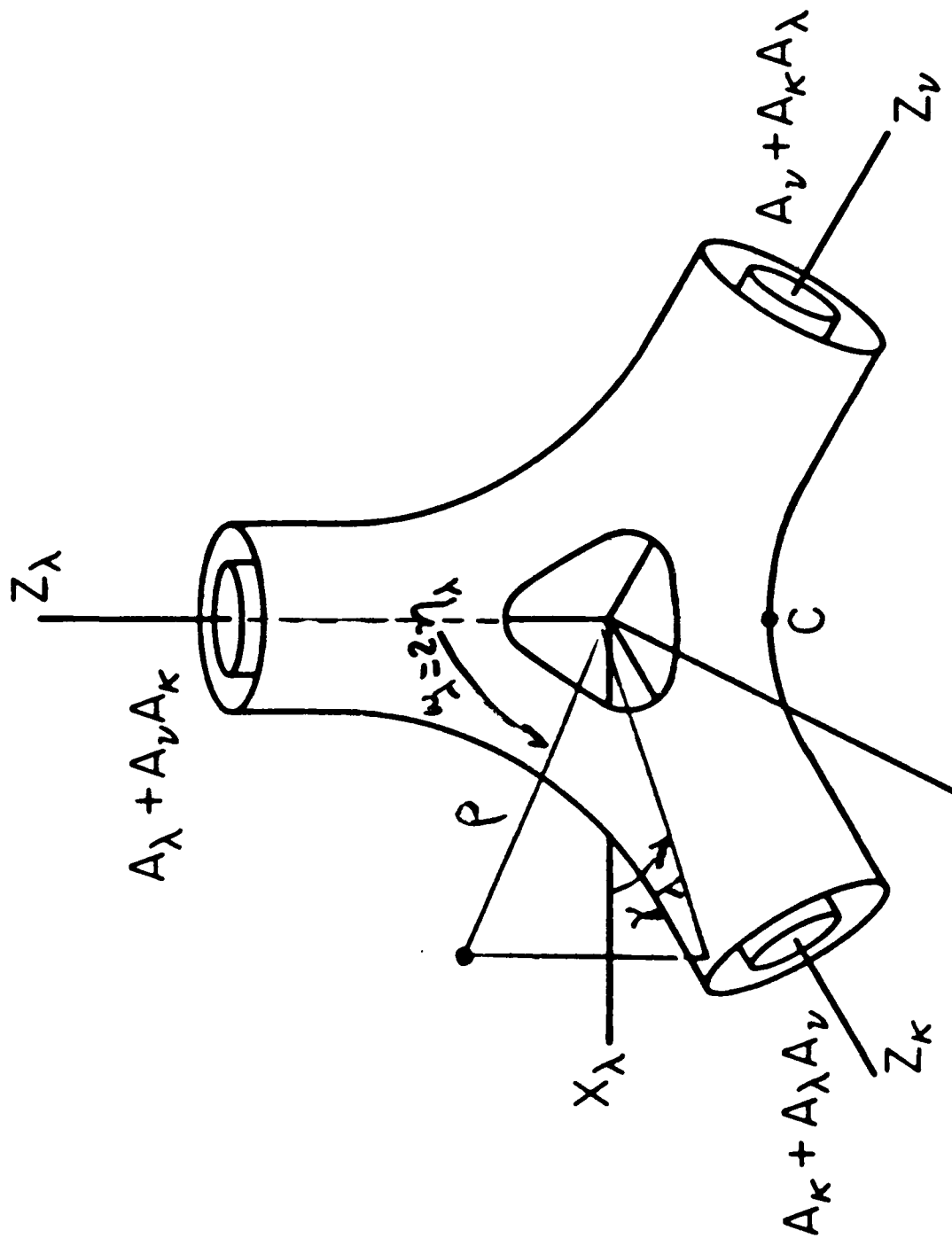


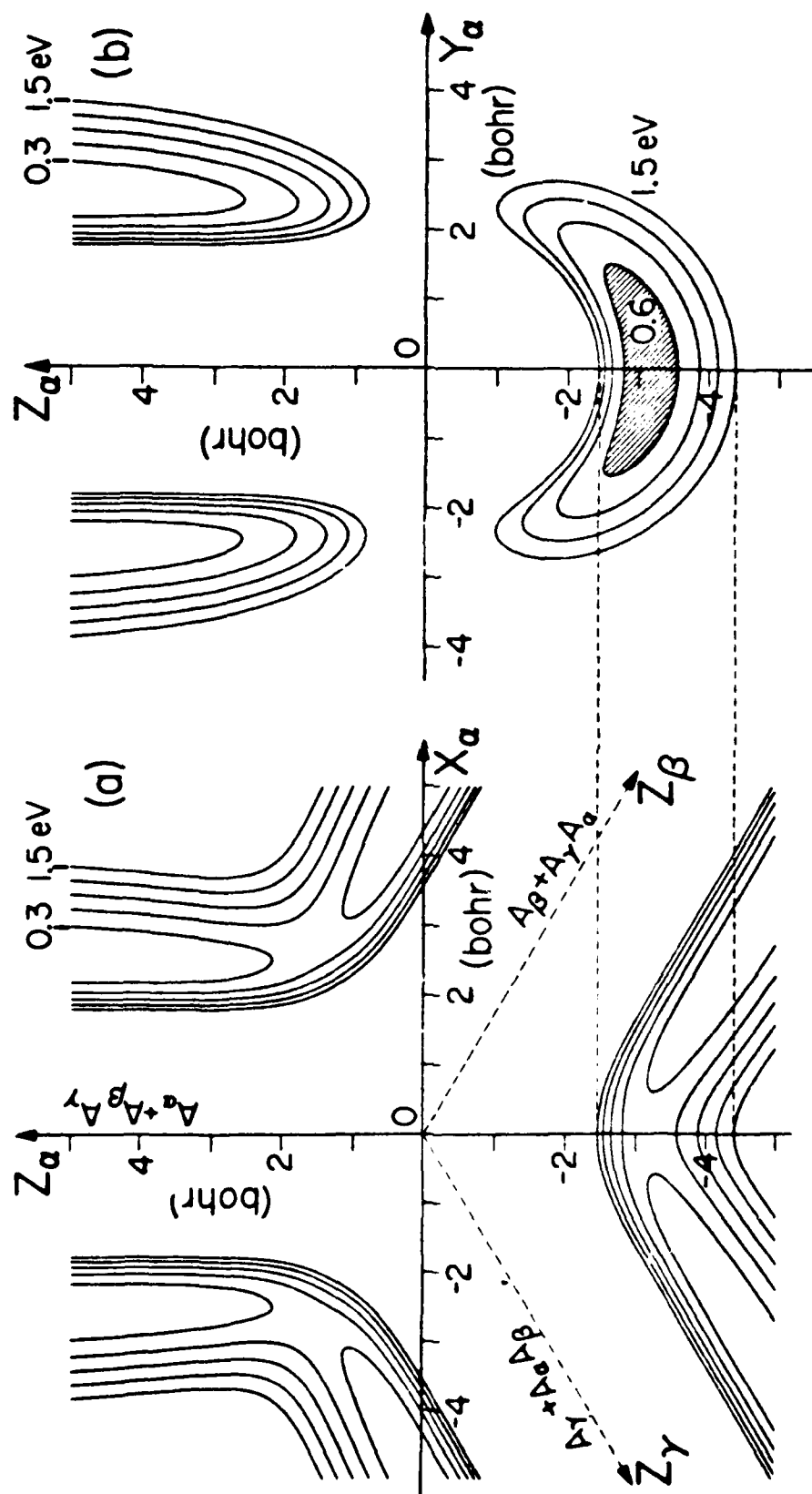
$$X_\alpha = \rho \sin \omega_\alpha \cos \gamma_\alpha$$

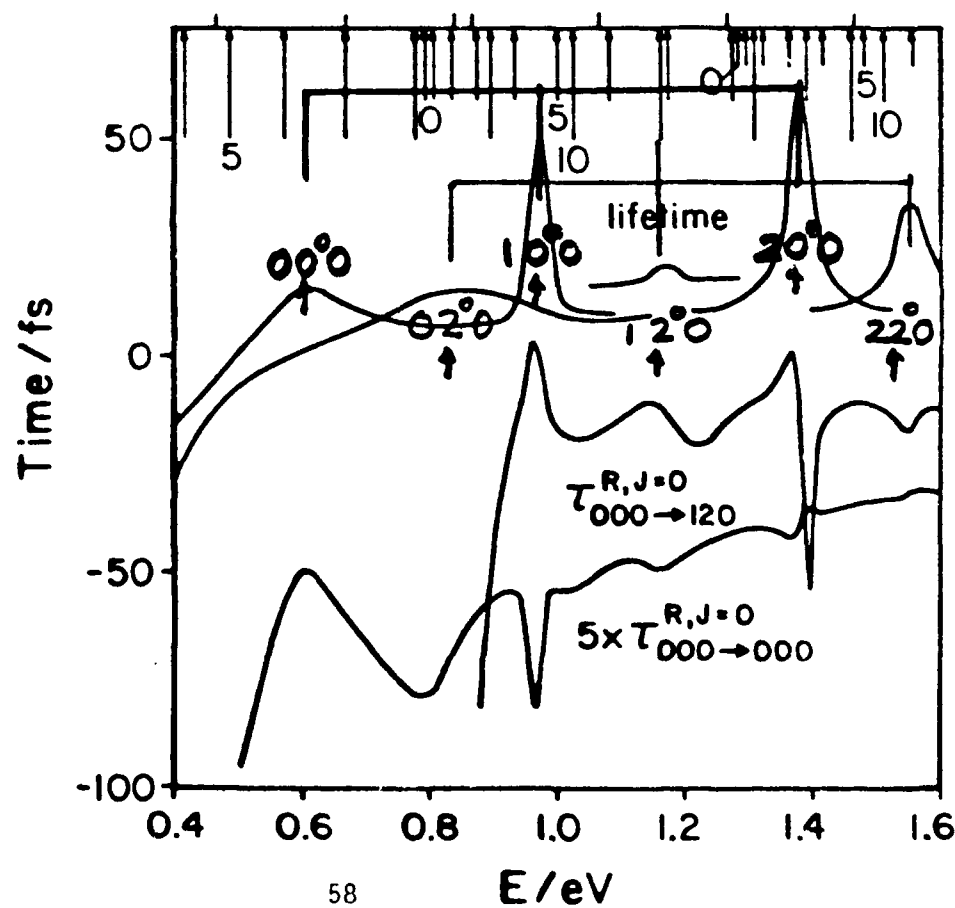
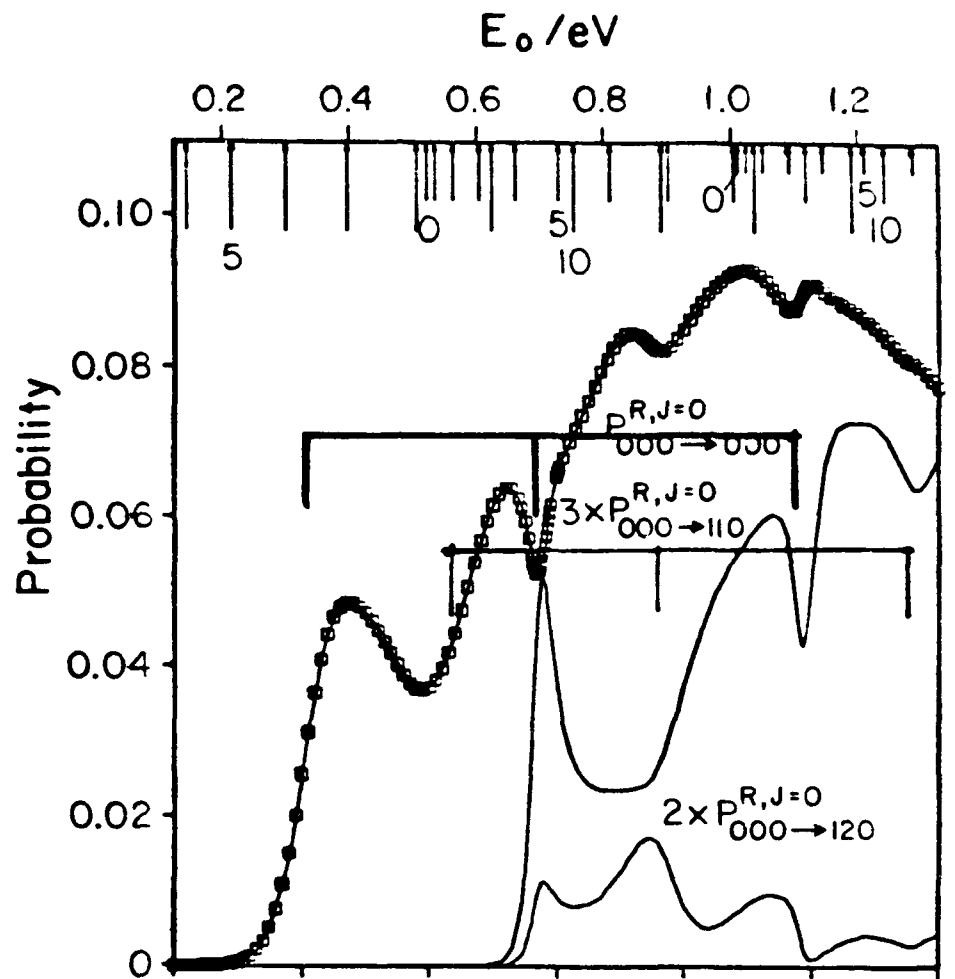
$$Y_\alpha = \rho \sin \omega_\alpha \sin \gamma_\alpha$$

$$Z_\alpha = \rho \cos \omega_\alpha$$

"Big Bang" picture







FORMULAS FOR CALCULATING DISTINGUISHABLE ATOM TRANSITION PROBABILITIES

$$j_{\text{even}} \rightarrow j_{\text{even}} \quad \left| \frac{1}{\sqrt{3}} S_{A_1} - \sqrt{\frac{2}{3}} S_E \right|^2$$

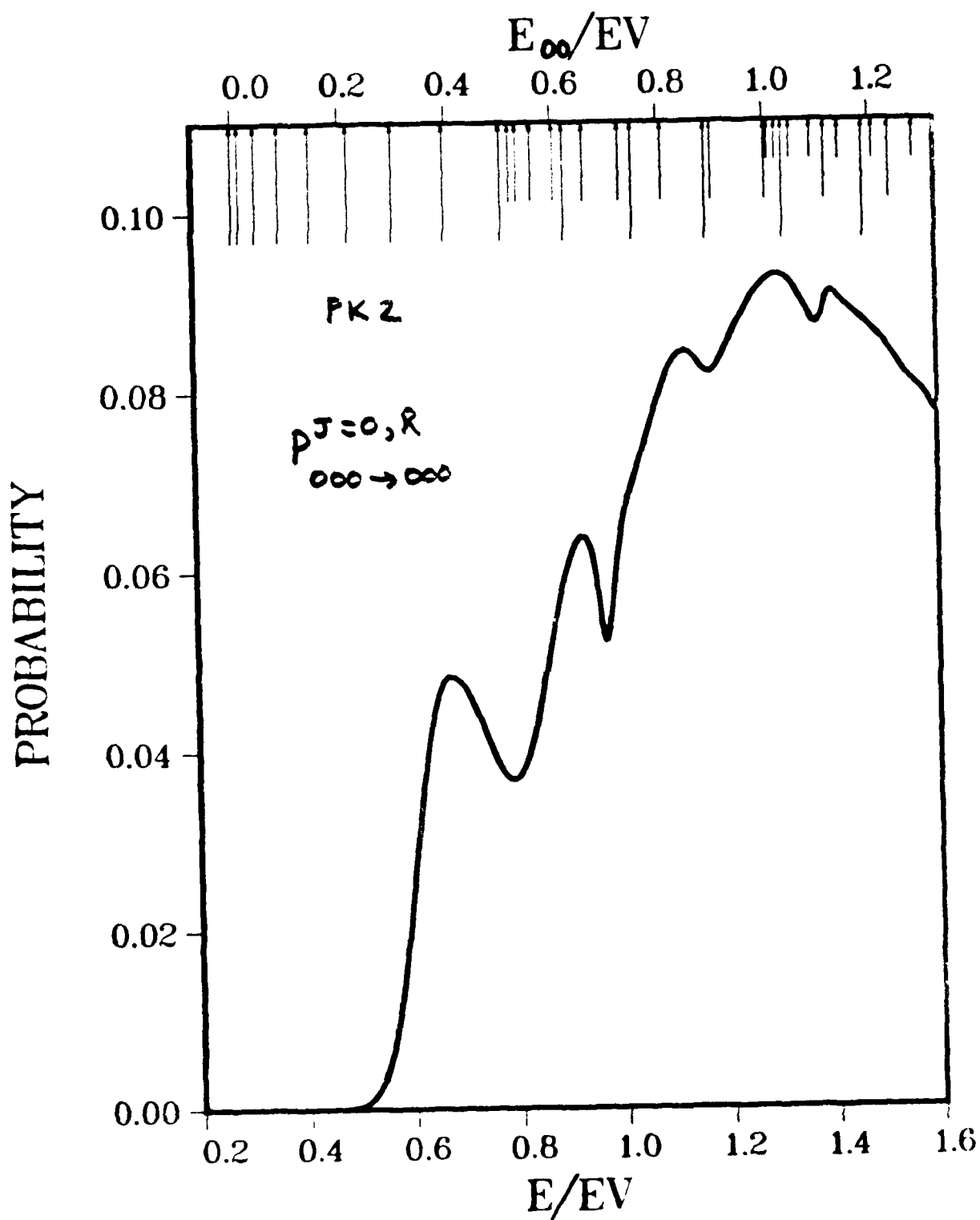
$$j_{\text{even}} \rightarrow j_{\text{odd}} \quad \left| \frac{1}{\sqrt{3}} S_E \right|^2$$

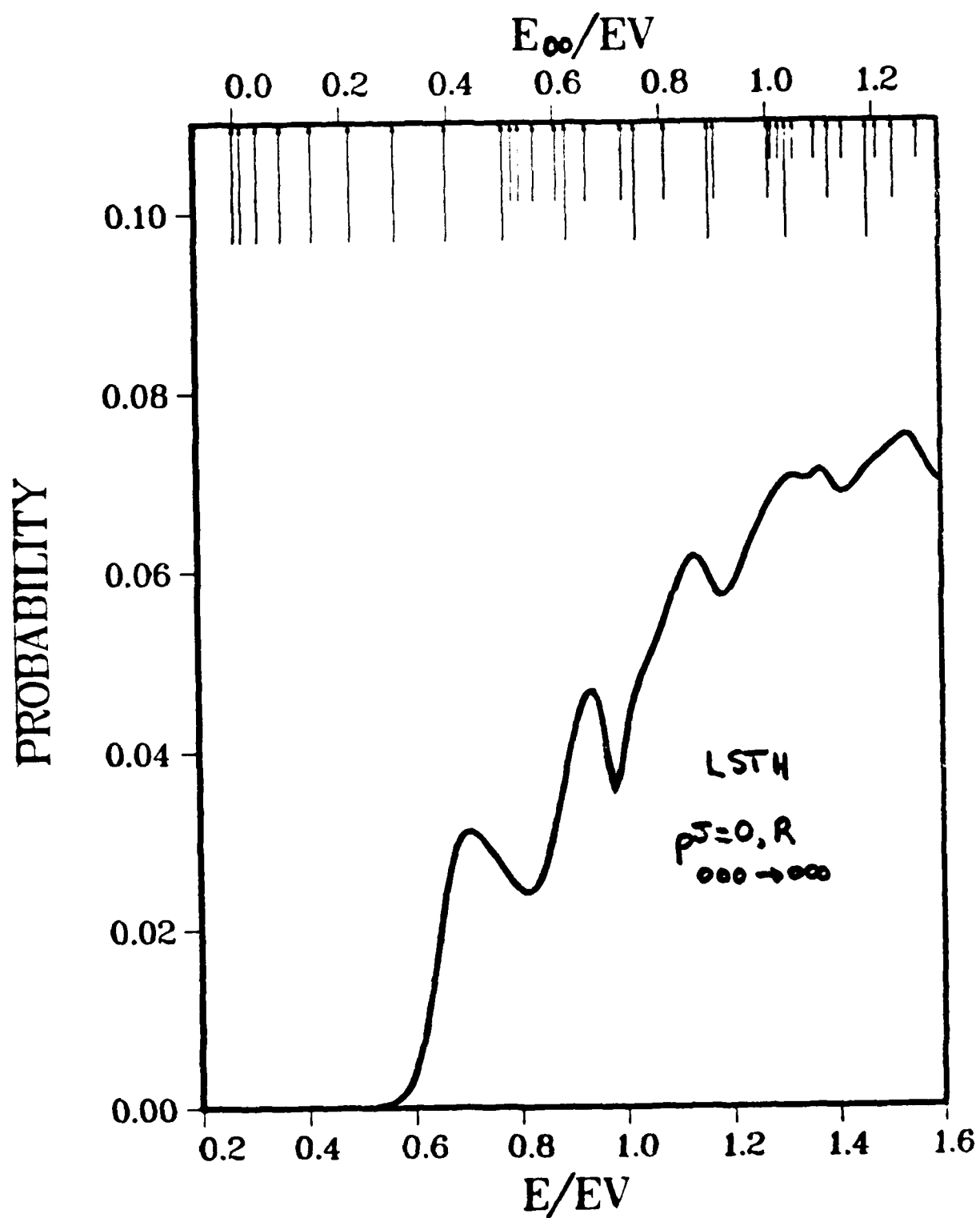
$$j_{\text{odd}} \rightarrow j_{\text{even}}$$

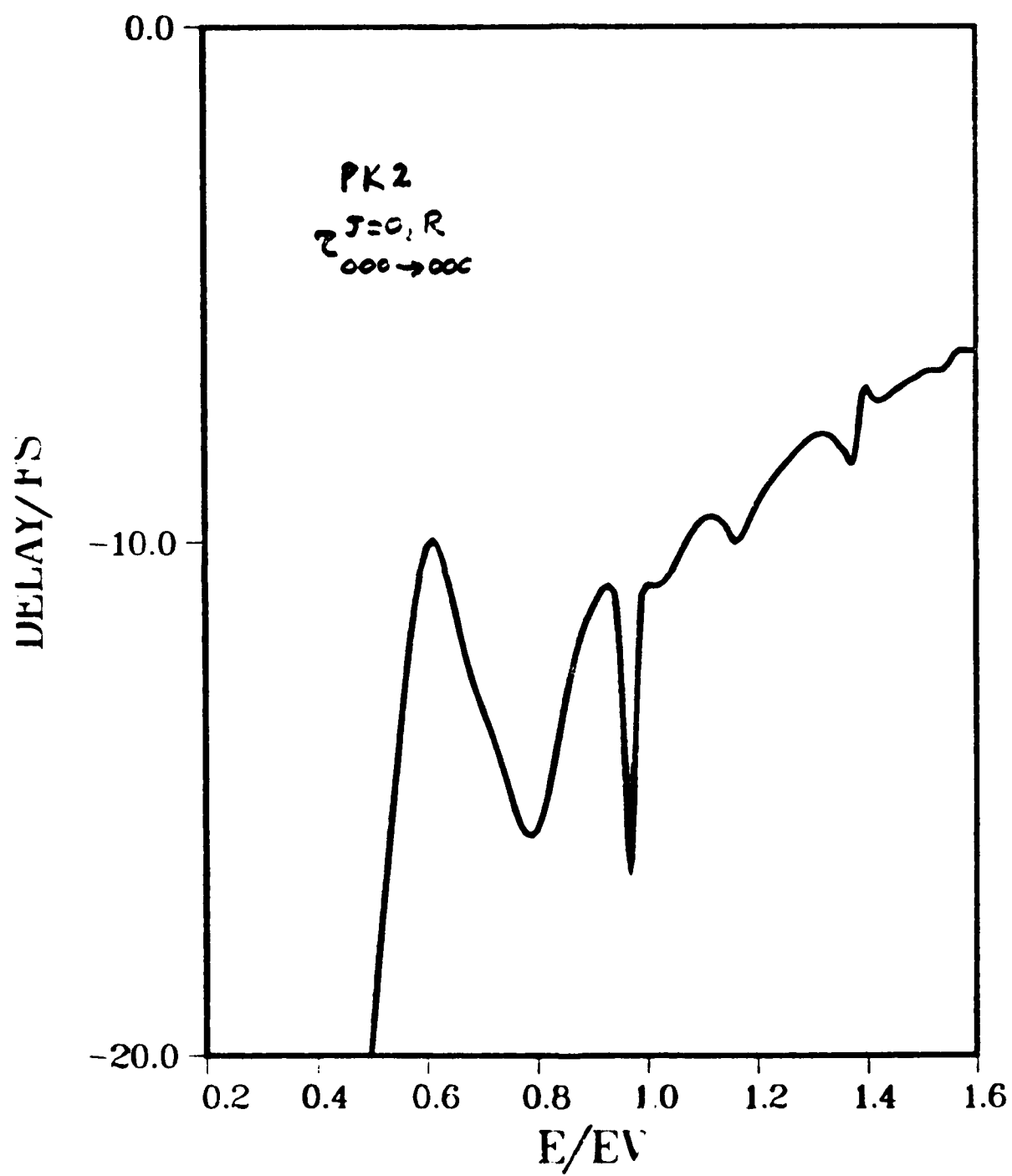
$$j_{\text{odd}} \rightarrow j_{\text{odd}} \quad \left| \frac{1}{\sqrt{3}} S_{A_2} - \sqrt{\frac{2}{3}} S_E \right|^2$$

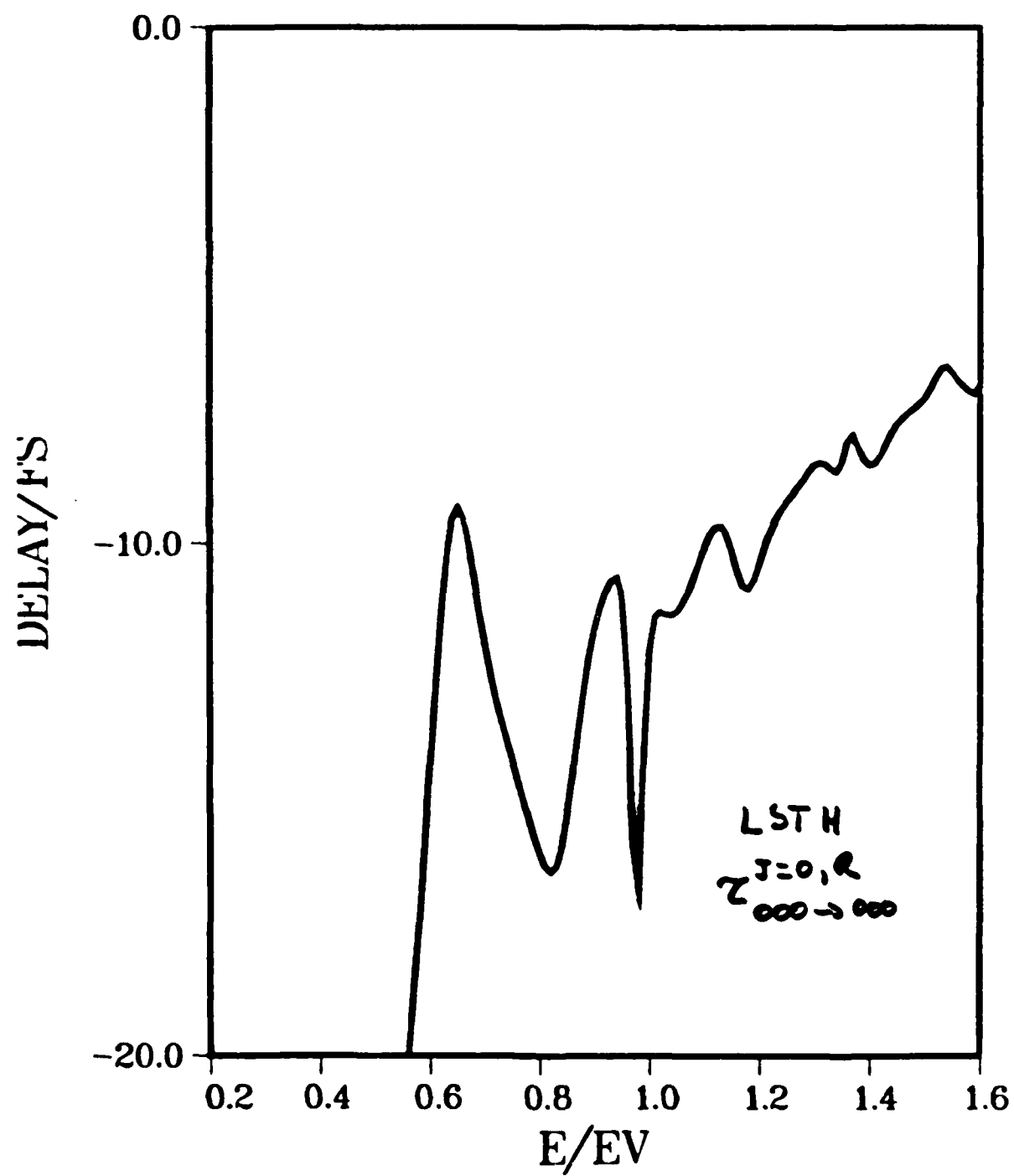
COLLISION LIFE-TIME MATRIX

$$Q = i\hbar \sum \frac{dS^{\dagger}}{dE}$$



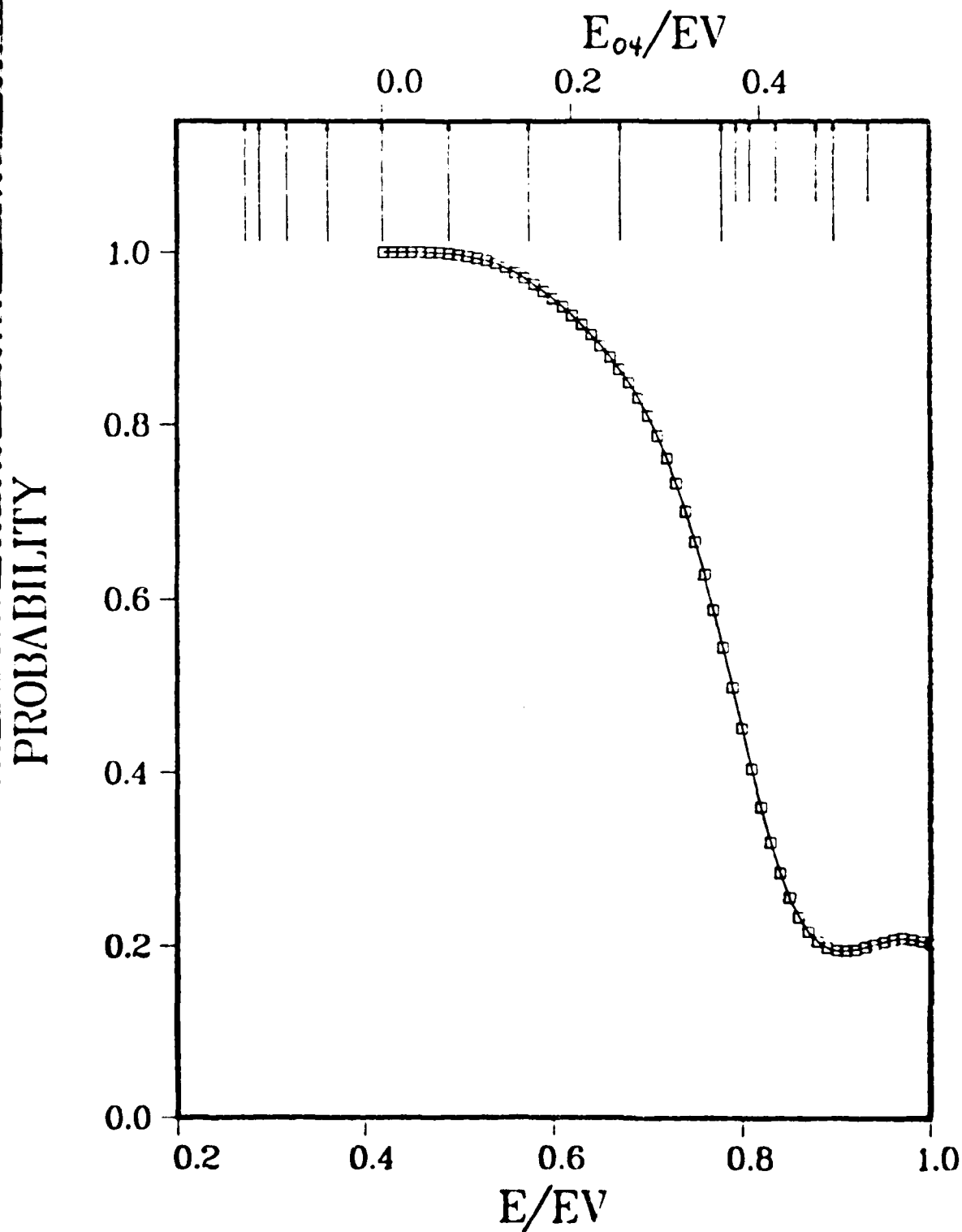




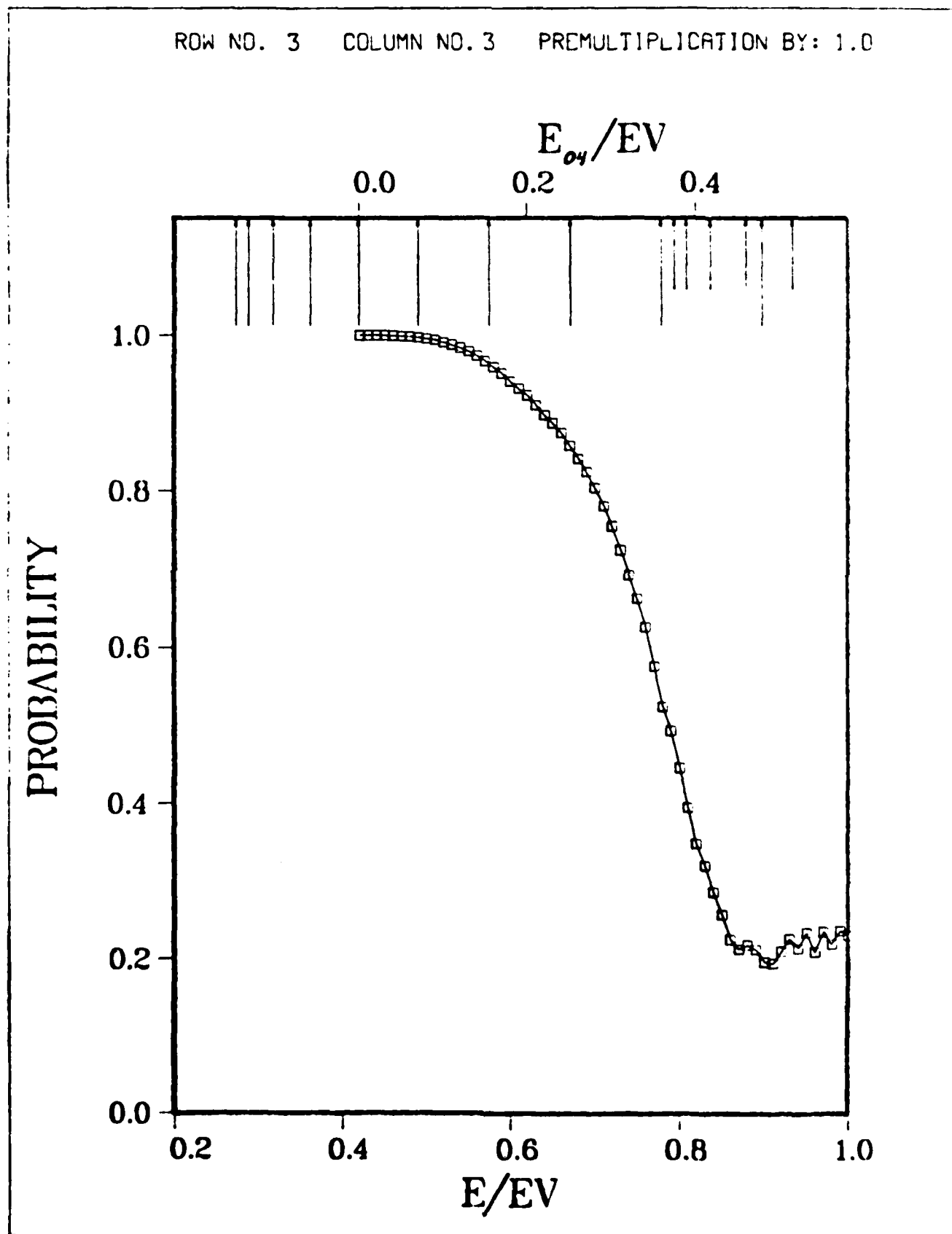


Hipes results PKII #6 state A, J=0 50w_A/150w_B mesh

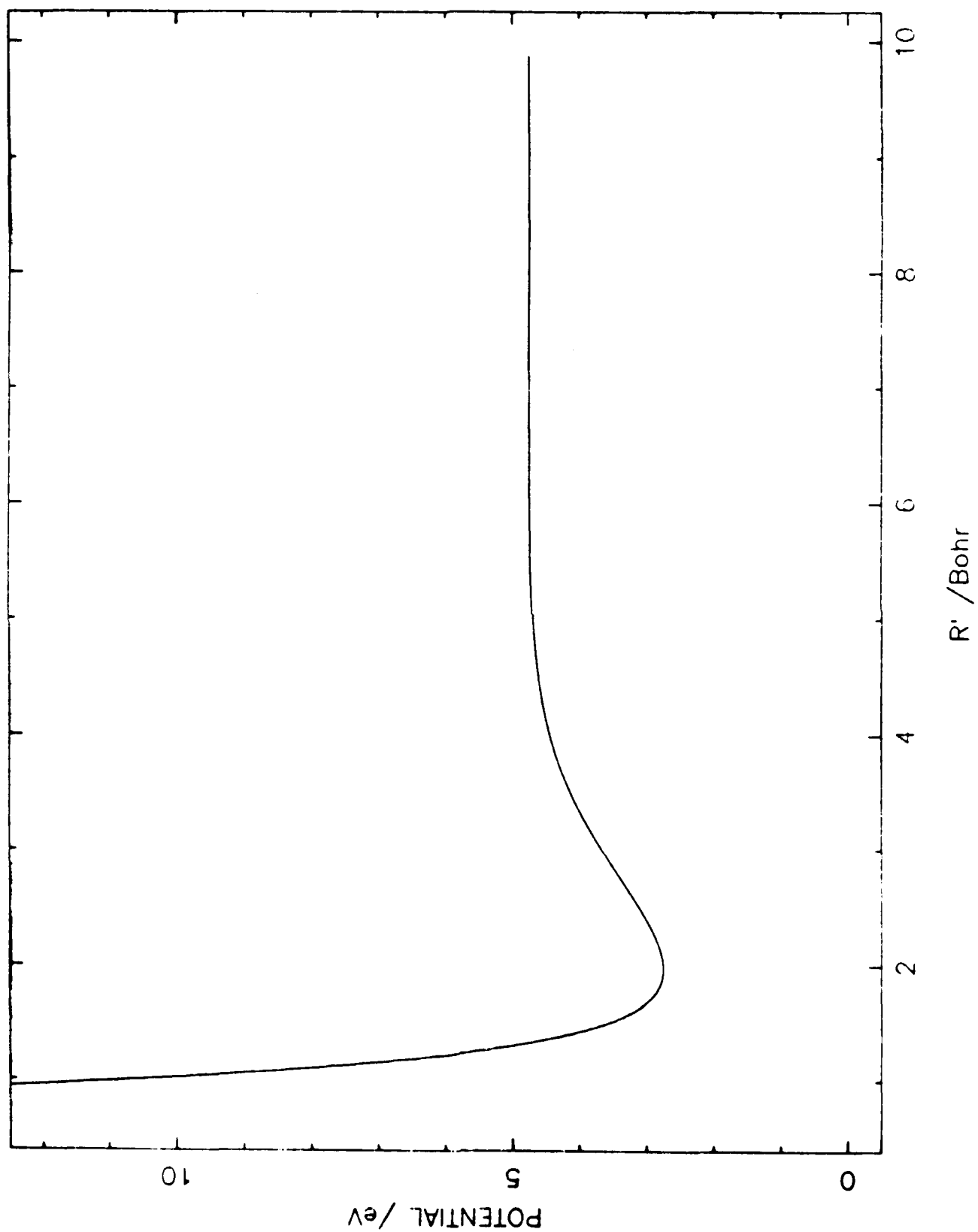
ROW NO. 3 COLUMN NO. 3 PREMULTIPLICATION BY: 1.0



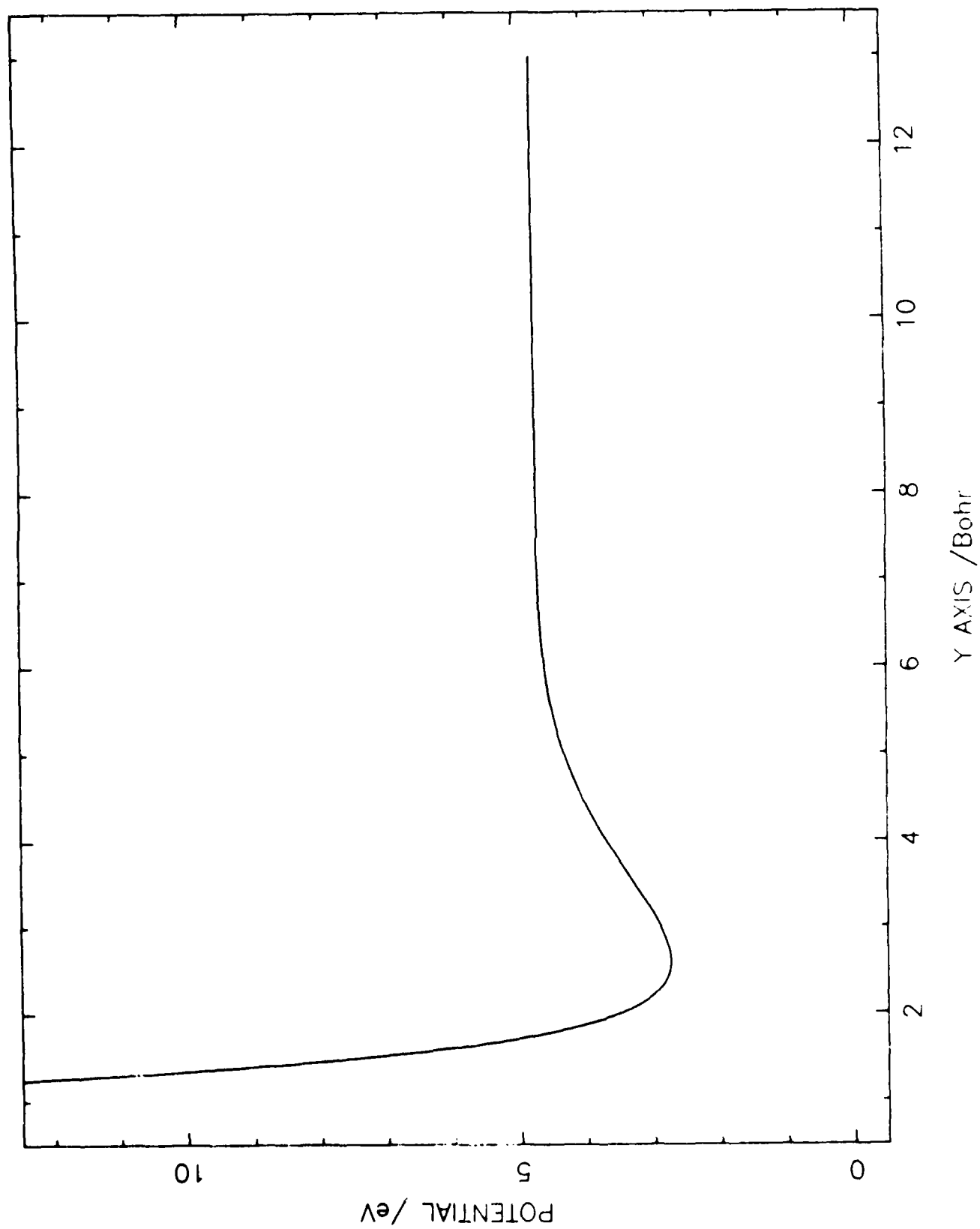
Cuccaro's results PKII 14 States H_1 $J=0$ 751m, by 100's mcs, 21 primitives
(error in overlap matrix between internal + asymptotic regions)



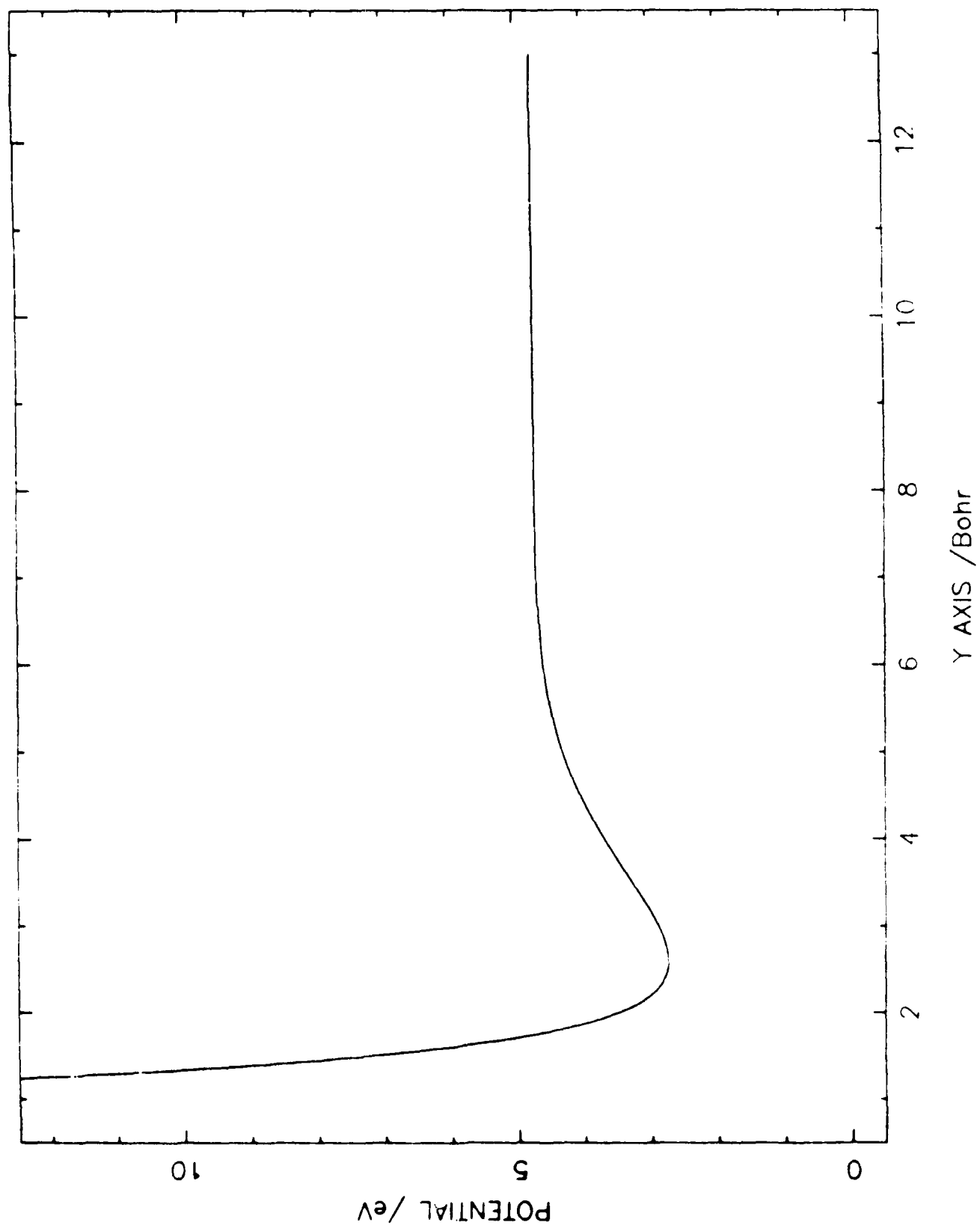
EQUALATERAL TRIANGLE H3



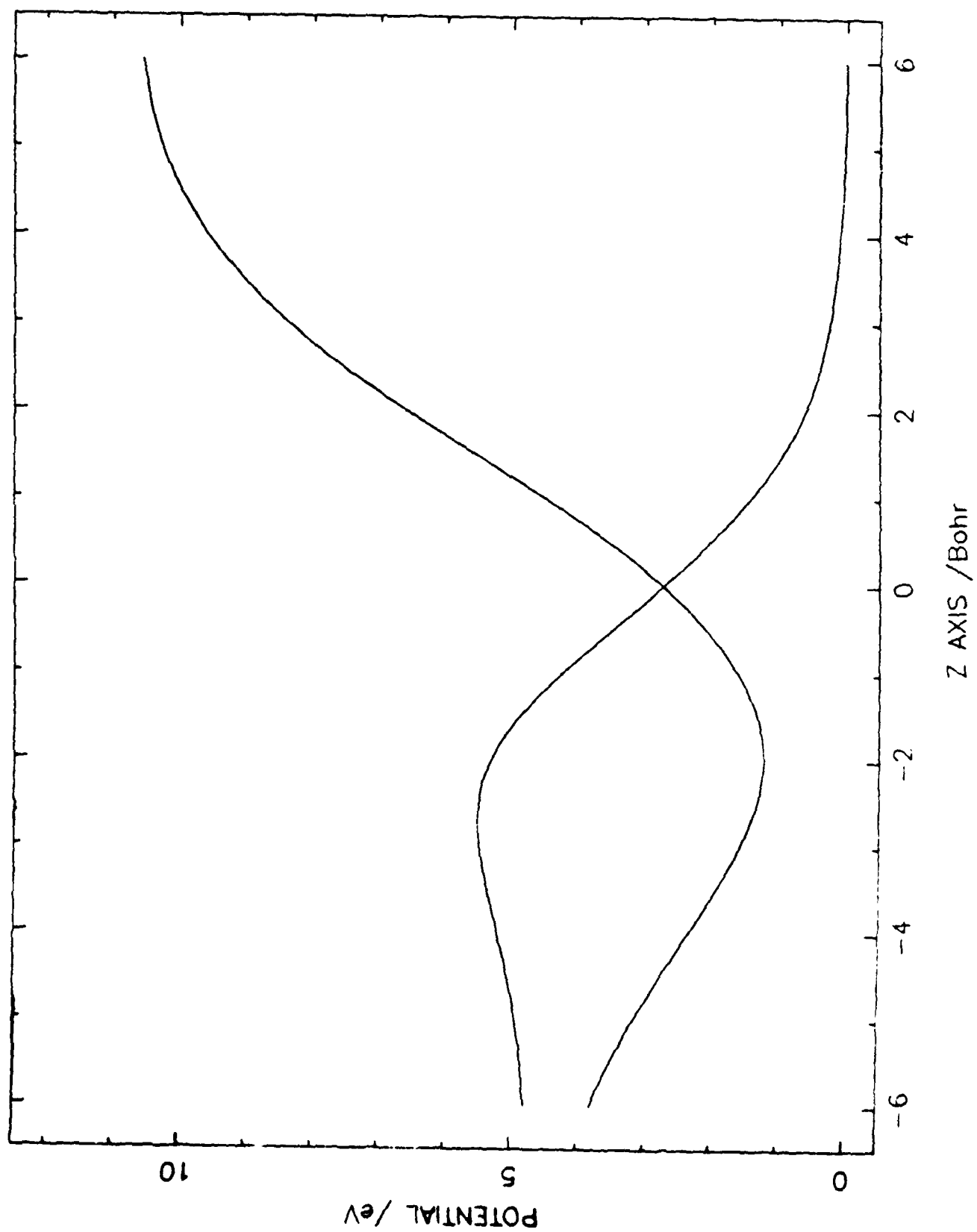
WITH $X=0.0$ Bohr AND $Z=0.0$ Bohr



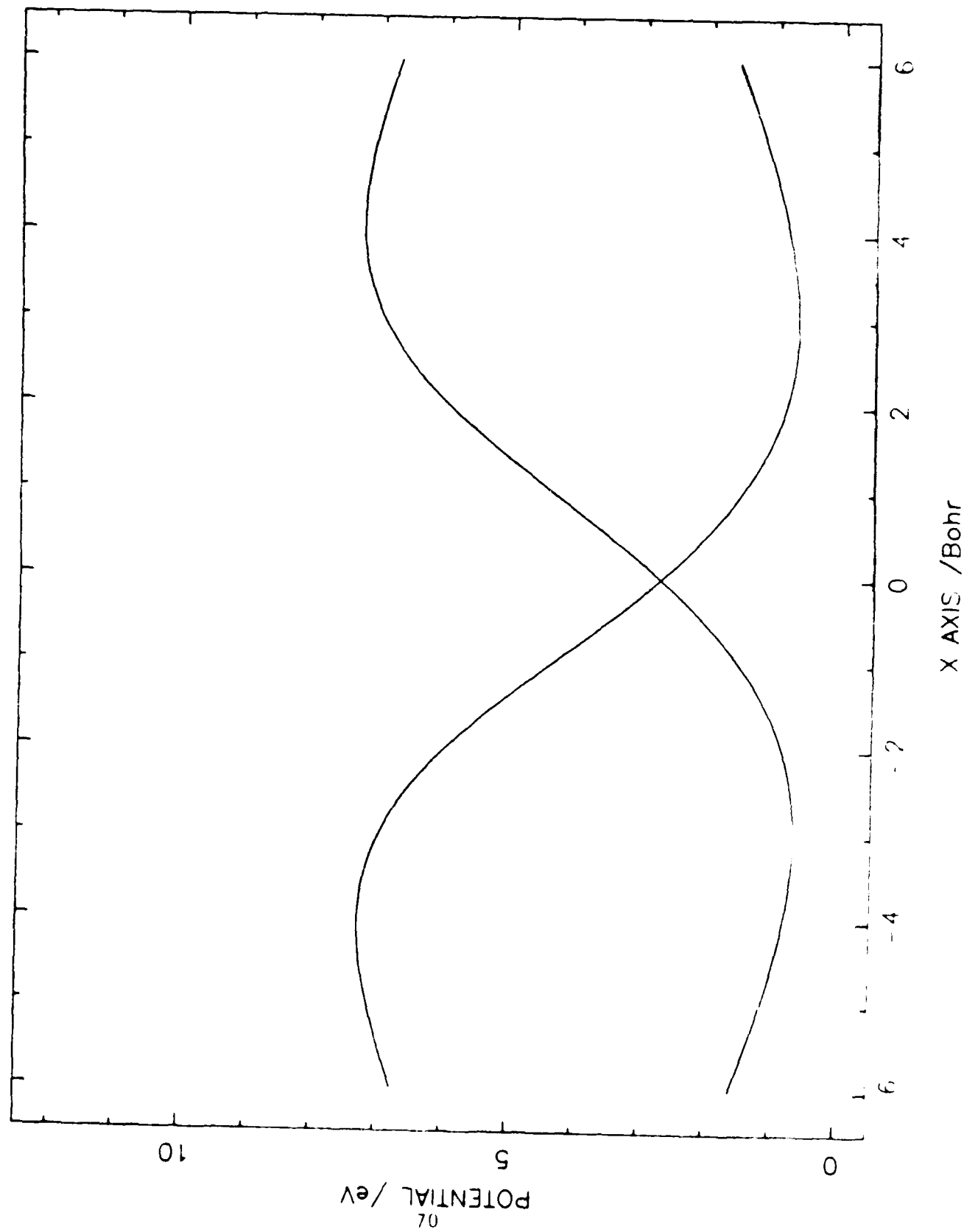
WITH $X=0.0$ Bohr AND $Z=0.0$ Bohr

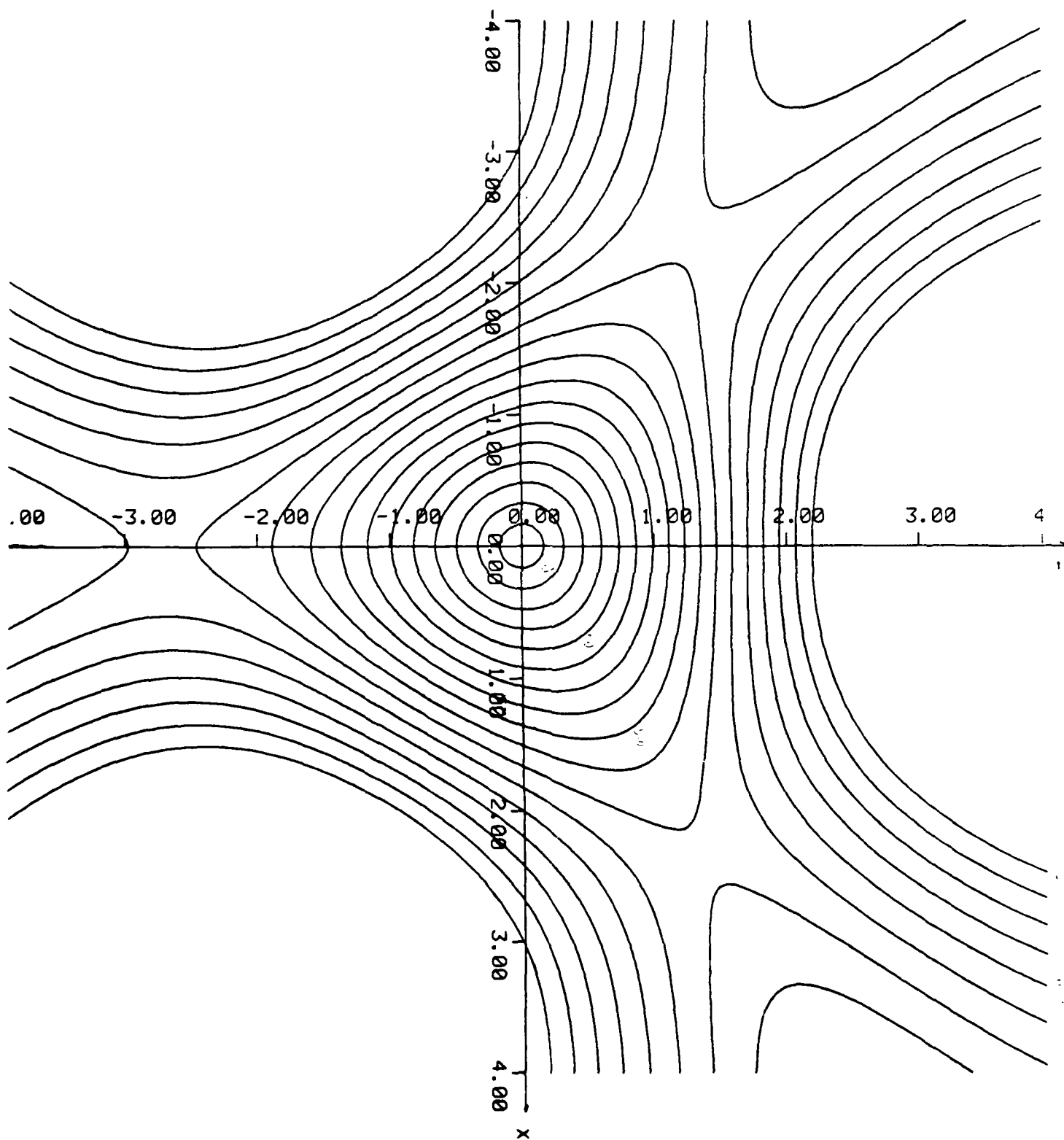


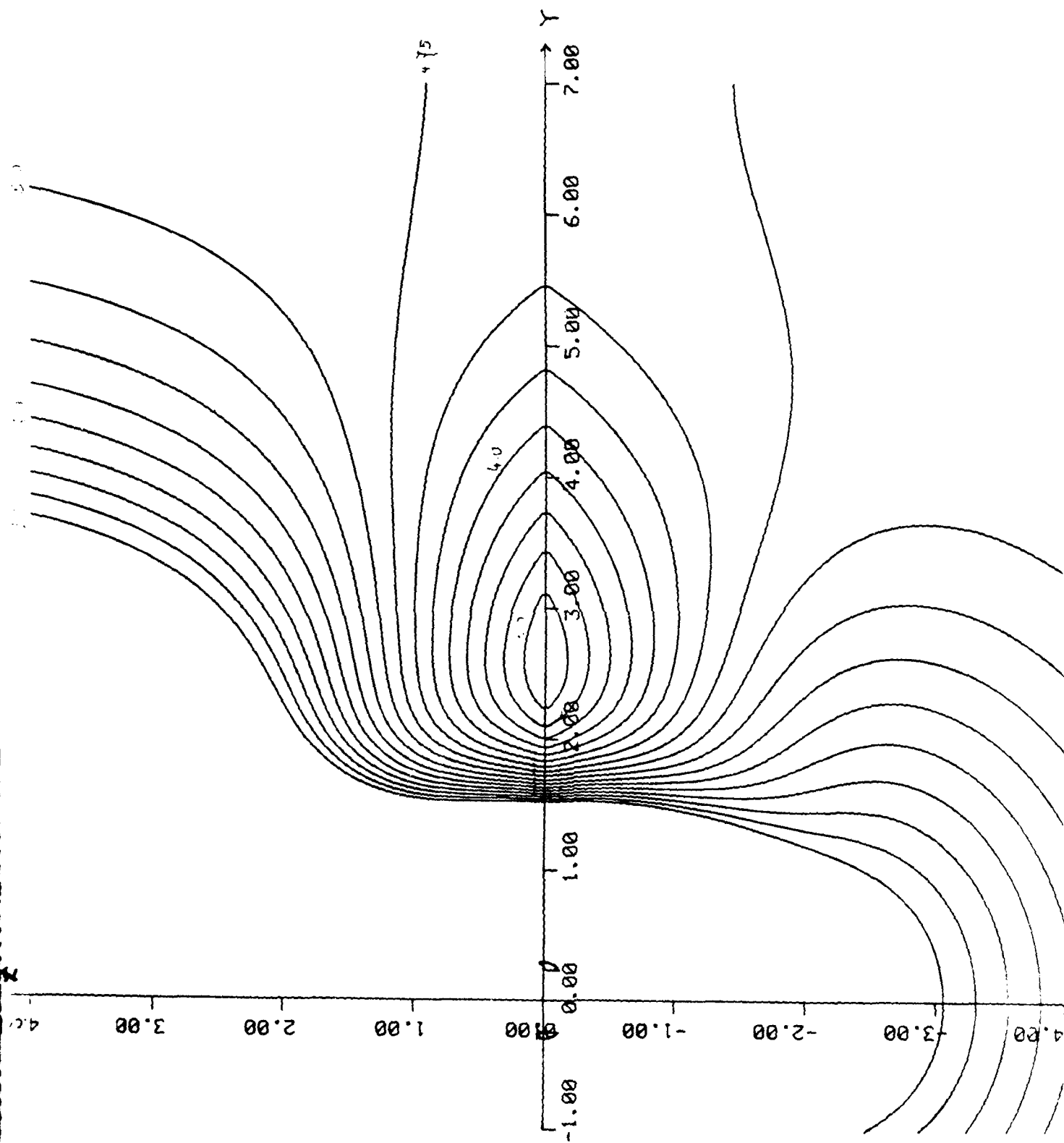
CONICAL INTERSECTION WITH $Y=Y_{\min}$ AND $X=0.0$ Bohr

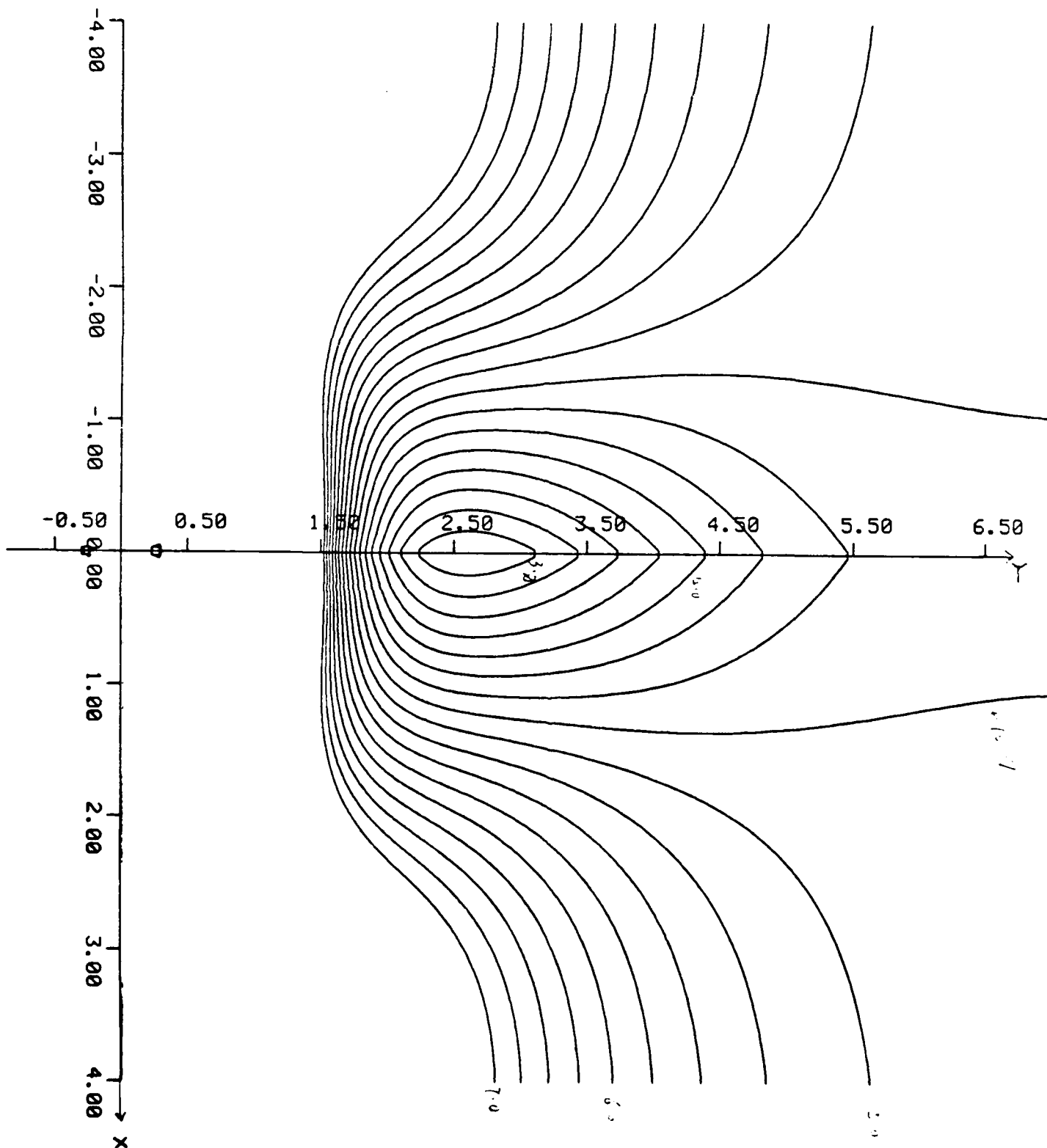


CONICAL INTERSECTION WITH $Y=Y_{\min}$ AND $Z=0.0$ Bohr









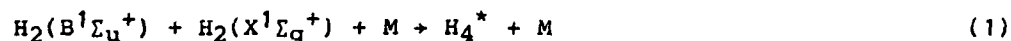
V_2
 2.50 3.50
 4.50 5.50
 6.50 7.00

CHARACTERIZATION OF TETRAHYDROGEN VIA STATE-SELECTED EXCITATION OF H₂

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The four-center H₄ system has been the subject of theoretical studies since the late sixties, primarily due to interest in the relationship of the ground state hypersurface to the H₂ + D₂ → 2HD exchange reaction.^{1,2,3} Investigations into the nature of the excited state(s) of such system have been limited in number even though SCF-MO-CI calculations in 1976 by Goddard and Csizmadia indicated the existence of a bound "excimer state."⁴ Recently, however, Nicolaides et al., using an extension of their modeling work on rare gas hydrides⁵ have predicted the existence of a bound singlet excited state of H₄ and have extended this analogy to the (H₂)₃ and (H₂)₅ clusters.^{6,7}

The theoretical studies of Refs. 6 and 7 predict that the bound state of H₄ arises from the reaction of molecular hydrogen in its ground state with H₂ that has been excited to the B(¹Σ_u⁺) state.



Further, the stable excited state is predicted to be produced only when the B¹Σ_u⁺ state precursor has sufficient "ionic" character for reaction with H₂(X). This is predicted to occur for v > 3 in the upper state.^{6,7}

Quenching studies of HD(B,v) performed by Atkins, Moore, and coworkers⁸⁻¹⁰ show an unusually large quenching cross section (79Å²) for H₂. This has led to further speculation that formation of a complex is involved. The H₂(B) state in v' = 3 has sufficient energy to dissociate itself as well as an H₂ collision partner:



Hence, quenching of H₂(B) by H₂ may be highly reactive with H-atoms as the products.

The goal of our experimental program is to produce H₂(B,v) in a supersonic jet by several techniques, provide a sufficient number of collisions with H₂ to produce H₄^{*}, stabilize the H₄^{*}, and probe for its existence and molecular properties. Four different methods have been chosen to produce H₂(B,v) in the jet: 1) energy transfer from Ar^{*} resonance states (1048Å, 1066Å lines) in Ar/H₂ mixtures via discharge production of Ar^{*} in the nozzle expansion region; 2) energy transfer from Ar^{*} resonance states in Ar/H₂ mixtures via resonant excitation of Ar^{*} with a VUV discharge lamp; 3) direct three photon laser excitation of H₂(B,v) at the nozzle throat; and 4) direct single photon laser excitation of H₂(B) via generation of tunable VUV radiation from third harmonic generation in rare gases.

The primary reason for using a supersonic molecular beam to produce H_4^* is to provide a locally high density but optically thin source of H_2 for direct VUV excitation of the $H_2(B)$ state as well as collisional production and stabilization of H_4^* . Three primary criteria must be met by the source:

1. There must be sufficient collisions in the expansion beyond the nozzle throat for collisional quenching of $H_2(B)$ to occur at a rate at least comparable to that for spontaneous radiation.
2. When energy transfer from Ar^* to H_2 is employed there must be sufficient collisions beyond the nozzle throat for Ar^* to be quenched by H_2 .
3. Formation of stabilized H_4^* is a three-body process. Hence, sufficient collisions must occur in the excitation region between the colliding $H_2(B) - H_2$ complex and a third body (H_2 or Ar).

An analysis of the nozzle flow characteristics (Figure 1) show that $H_2(B)$ must be excited within 0.9 mm of the nozzle throat in order for conditions 1 to 3 to be satisfied.

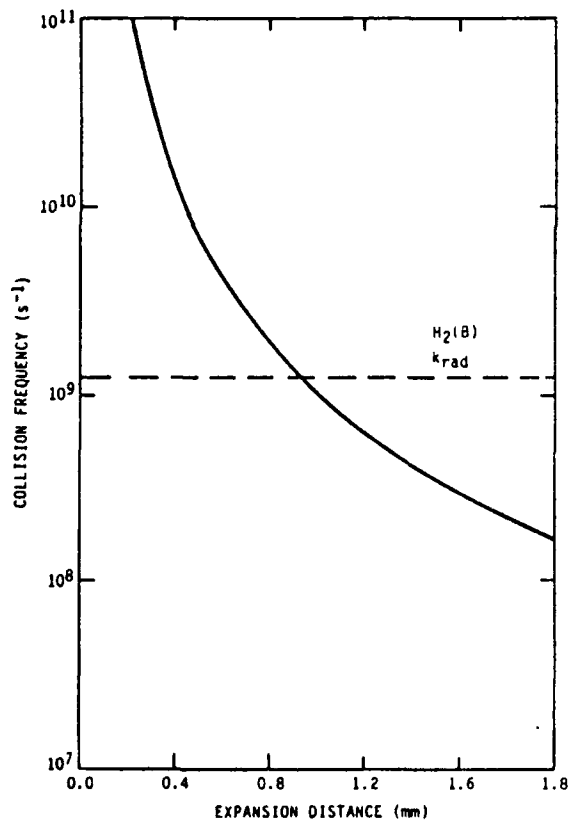


Figure 1. $H_2(B)$ Collision Frequency as a Function of Distance from the Nozzle Throat

The calculations of Nicolaides and coworkers⁵⁻⁷ show that H_4^* is bound by 3.1 eV with respect to dissociation to form $H_2(B)$ and H_2 . However, they also have shown that the complex is bound by 1.86 eV with respect to dissociation along the $H^- + H_3^+$ coordinate. Hence, photolysis of H_4^* may produce $H_3^+ + H^-$, $H_3 + H$, or $H_2(B) + H_2$. A careful selection of photolysis wavelengths may result in selective excitation into any of these channels. In our experimental effort we will be using a range of photolysis wavelengths in order to excite the channel leading to $H_2(B) + H_2$. We are also considering detection schemes to observe ionic dissociation pathways and $H_2(B)$ quenching collisions which produce atomic hydrogen. Observation of H_4^* may also be accomplished via detection of passive emission from the radiating excimer, if such radiation does indeed exist.

Photolysis of H_4^* will initially be attempted using a broadband flash-lamp source ($\lambda = 190$ to 3000 nm). A solar blind PMT will be used to detect $H_2(B)$ emission

resulting from the photolysis. Use of this broadband source is desirable in order to minimize the time required for a long search for appropriate photolysis wavelengths. As $H_2(B)$ emission is observed the flashlamps will be filtered to narrow the effective photolysis bandwidths until a spectral range is defined over which more selective laser-based photolysis studies can be conducted.

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2. Wilson, C.W., Jr. and Goddard, W.A., III, "Ab Initio Calculations on the $H_2 + D_2 = 2HD$ Four Center Exchange Reaction I: Elements of the Reaction Surface," Chem. Phys. 51, 716 (1969).
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7. Nicolaides, C.A., Petsalakis, I.D., and Theodorakopoulos, G., "Theory of Chemical Reactions of Vibronically Excited $H_2(B^1\Sigma_u^+)$. III. Formation of Bound Excited States of the $(H_2)_2$, $(H_2)_3$, and $(H_2)_5$ Clusters," J. Chem. Phys. 81, 748 (1984).
8. Fink, E.H., Akins, D.L., and Moore, C.B., "Energy Transfer in Monochromatically-Excited Hydrogen ($B^1\Sigma_u^+$). I. Excitation Processes, Electronic Quenching, and Vibrational Energy Transfer," J. Chem. Phys. 56, 900 (1972).
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10. Fink, E.H., Wallach, D., and Moore, C.B., "Near-Resonant Electronic Energy Transfer from Argon to Hydrogen," J. Chem. Phys. 56, 3608 (1972).

CHARACTERIZATION OF TETRAHYDROGEN VIA
STATE-SELECTED EXCITATION OF H₂

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TO

HIGH ENERGY DENSITY MATTER CONFERENCE
ROSSLYN, VIRGINIA

12-13 MAY 1987



PROGRAM OBJECTIVES

- PRODUCE AND CHARACTERIZE H_4^*
- EXPERIMENTAL APPROACH TO H_4 STUDIES
 - PRODUCTION OF $H_2(B)$
 - STABILIZATION OF $H_2(B)$ - H_2 COMPLEX AND RELAXATION OF H_4^*
 - DETECTION OF H_4
- EXPERIMENTAL OBSERVATIONS
 - THREE PHOTON EXCITATION OF $H_2(B)$
 - ENERGY TRANSFER FROM Ar^* (106.6 nm) to $H_2(B)$



TETRAHYDROGEN: NICOLAIDES et al.

- STABLE EXCIMER OF $H_2(B) + H_2$
 - FORMED WHEN $H_2(B)$ IN STATE OF "MAXIMUM IONICITY" CORRESPONDING TO $v' = 3$ OF B-STATE
 - STABILITY OF H_4

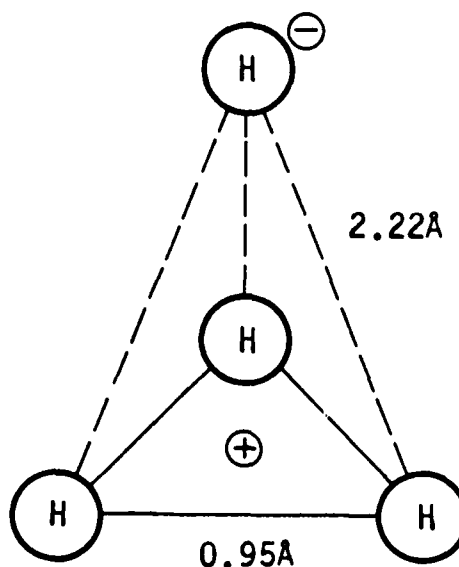
$$H_4 \rightarrow H_2(B) + H_2 \quad \Delta E = -2.48 \text{ eV}$$

$$H_4 \rightarrow H_3^+ + H^- \quad \Delta E = -1.86 \text{ eV}$$
 - VIBRATIONAL FREQUENCIES PROBABLY SIMILAR TO H_3^+

SYMMETRIC STRETCH: $\nu = 3185 \text{ cm}^{-1}$

BEND: $\nu = 2516 \text{ cm}^{-1}$

● GEOMETRY



EXPERIMENTAL APPROACH

- COLLISIONALLY QUENCH $H_2(B,v)$ WITH H_2 CLOSE TO THROAT OF SUPERSONIC JET
 - H_2 OPTICALLY THIN HENCE DIRECT EXCITATION POSSIBLE
 - COLLISION RATE NEAR THROAT SUFFICIENT FOR QUENCHING OF $H_2(B)$ TO EFFICIENTLY COMPETE WITH RADIATION
 - EXPANSION "COOLS" COMPLEX AND PROVIDES COLLISION-FREE REGION FOR CHARACTERIZATION
- PROVIDE DIFFERENT EXCITATION SOURCES FOR $H_2(B)$ TO MINIMIZE H_4 DESTRUCTION
 - DISCHARGE EXCITATION OF H_2/Ar MIXTURE
 - RESONANT EXCITATION OF H_2/Ar MIXTURE WITH Ar 1048Å AND 1066Å LINES
 - DIRECT VUV EXCITATION OF $H_2(B)$
 - THREE PHOTON EXCITATION OF $H_2(B)$



QUENCHING IN H₂ AND H₂/Ar

- H₂(B) QUENCHING BY H₂

- MOORE et al. $\sigma_{H_2} = 79 \text{ \AA}^2$

$$k_Q = \bar{c}\sigma \quad \bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

$$k_Q = 1.1 \times 10^{-9} \left(\frac{T}{300}\right)^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- QUENCHING CONDITION. $k_Q[H_2] = k_{\text{rad}}$

$$k_{\text{rad}} = 1.5 \times 10^9 \text{ s}^{-1}$$

$$[H_2] = 1.4 \times 10^{18} \text{ molecule cm}^{-3} \text{ AT } 300 \text{ K}$$

- Ar* QUENCHING BY H₂

- BOXALL et al. $\sigma = 48 \text{ \AA}^2$

$$k_Q = 1.9 \times 10^{-10} \left(\frac{T}{300}\right)^{1/2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

- QUENCH Ar* 1066 \text{ \AA} LINE: $k_{\text{rad}} = 1.2 \times 10^8 \text{ s}^{-1}$

$$[H_2] = 6.3 \times 10^{17} \text{ molecule cm}^3 \text{ AT } 300 \text{ K}$$

- IN Ar/H₂ MIXTURES $[H_2] \approx 1 \times 10^{18} \text{ molecule cm}^{-3}$ WILL QUENCH BOTH Ar* AND H₂(B)



MOLECULAR BEAM NOZZLE EQUATIONS

$$\frac{N}{N_0} = [1 + (\gamma + 1) M^2/2]^{1/(1-\gamma)}$$

$$\frac{T}{T_0} = [1 + (\gamma + 1) M^2/2]^{-1}$$

$$\bar{v} = \left(\frac{\gamma k T}{M}\right)^{1/2} M$$

WHERE M IS THE EXPANSION MACH NUMBER AND A FUNCTION OF (L/D)

L = DISTANCE DOWNSTREAM

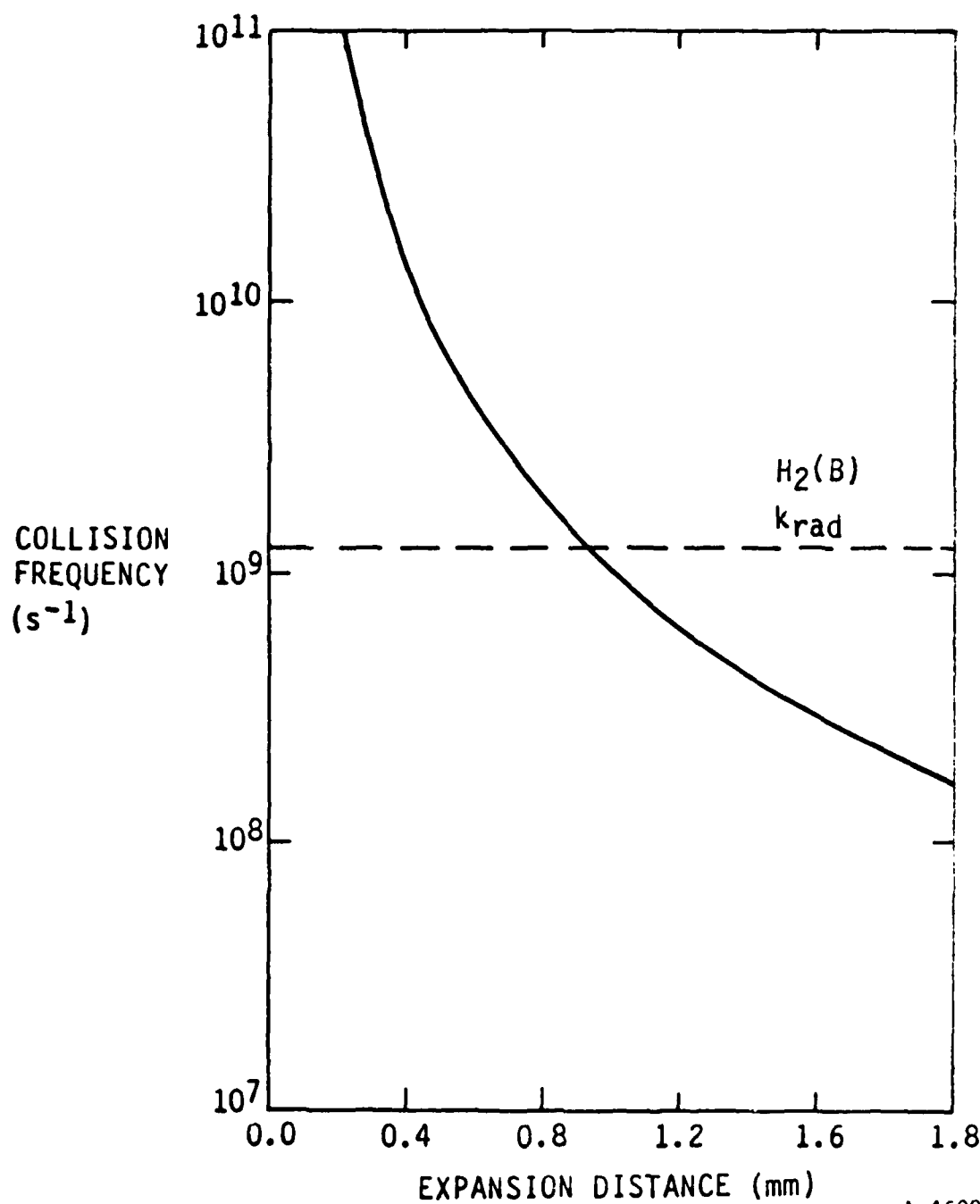
D = THROAT DIAMETER

- ANALYTICAL EXPRESSIONS FOR M VERSUS (L/D) FROM ANDERSON



$H_2(B)$ COLLISION FREQUENCY AS A FUNCTION OF DISTANCE FROM THE NOZZLE THROAT

250 μm DIAMETER NOZZLE, $P_{H_2} = 5 \text{ ATM}$

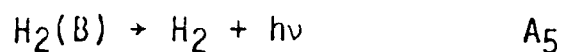
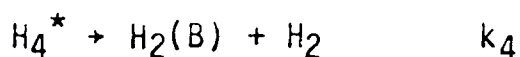
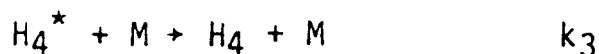
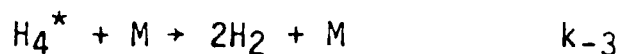
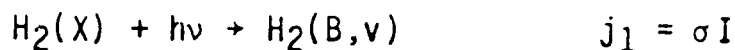


A-4608



STABILIZATION OF H_4^*

- LIFETIME OF $H_2(B) - H_2$ COMPLEX $10^{-10} - 10^{-12}s$



- H_4^* LIFETIME SHORT - STEADY-STATE SOLUTION APPROPRIATE

$$\frac{d[H_4]}{dt} = j_1[H_2] \left\{ \frac{\phi k_2[H_2]}{k_2[H_2] + A_5} \right\} \left\{ \frac{k_3[H_2]}{2k_3[H_2] + k_4} \right\}$$

- ESTIMATED H_4 FORMATION EFFICIENCIES/ $H_2(B)$

$$[H_2] = 10^{18} \text{ molecule cm}^{-3}$$

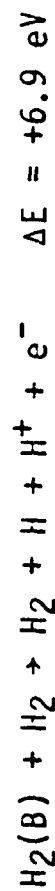
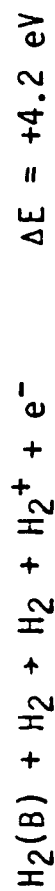
$k_4 \text{ (s}^{-1}\text{)}$	$H_4 \text{ EFFICIENCY}$
10^{10}	10^{-2}
10^{11}	10^{-3}
10^{12}	10^{-4}



RELAXATION OF H_4^*

- DYNAMICAL SIMULATIONS OF OTHER SYSTEMS (Ar-O₃) SHOW APPROXIMATELY 100 COLLISIONS SUFFICIENT TO RELAX COMPLEX SIGNIFICANTLY

- OTHER REACTIVE CHANNELS FOR H₂(B)



- H-ATOM FORMATION POSSIBLE CHANNEL



NO-A107 270

PROCEEDINGS OF THE HIGH ENERGY DENSITY MATTER (HEDM)
CONFERENCE HELD IN R. (U) AIR FORCE ASTRONAUTICS LAB
EDWARDS AFB CA W J LAUDERDALE ET AL. SEP 87

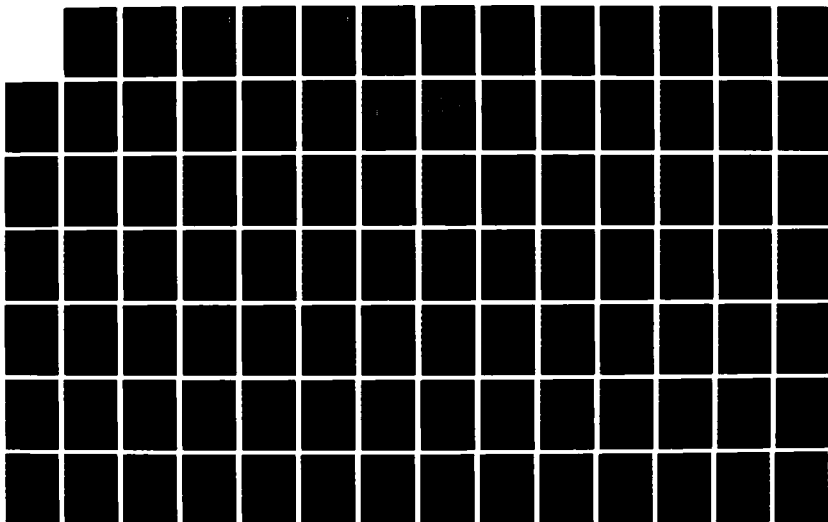
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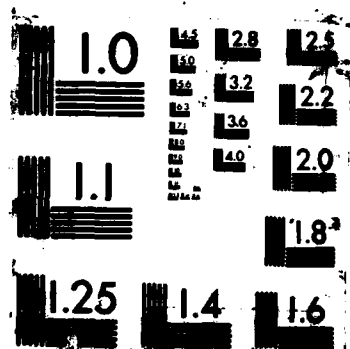
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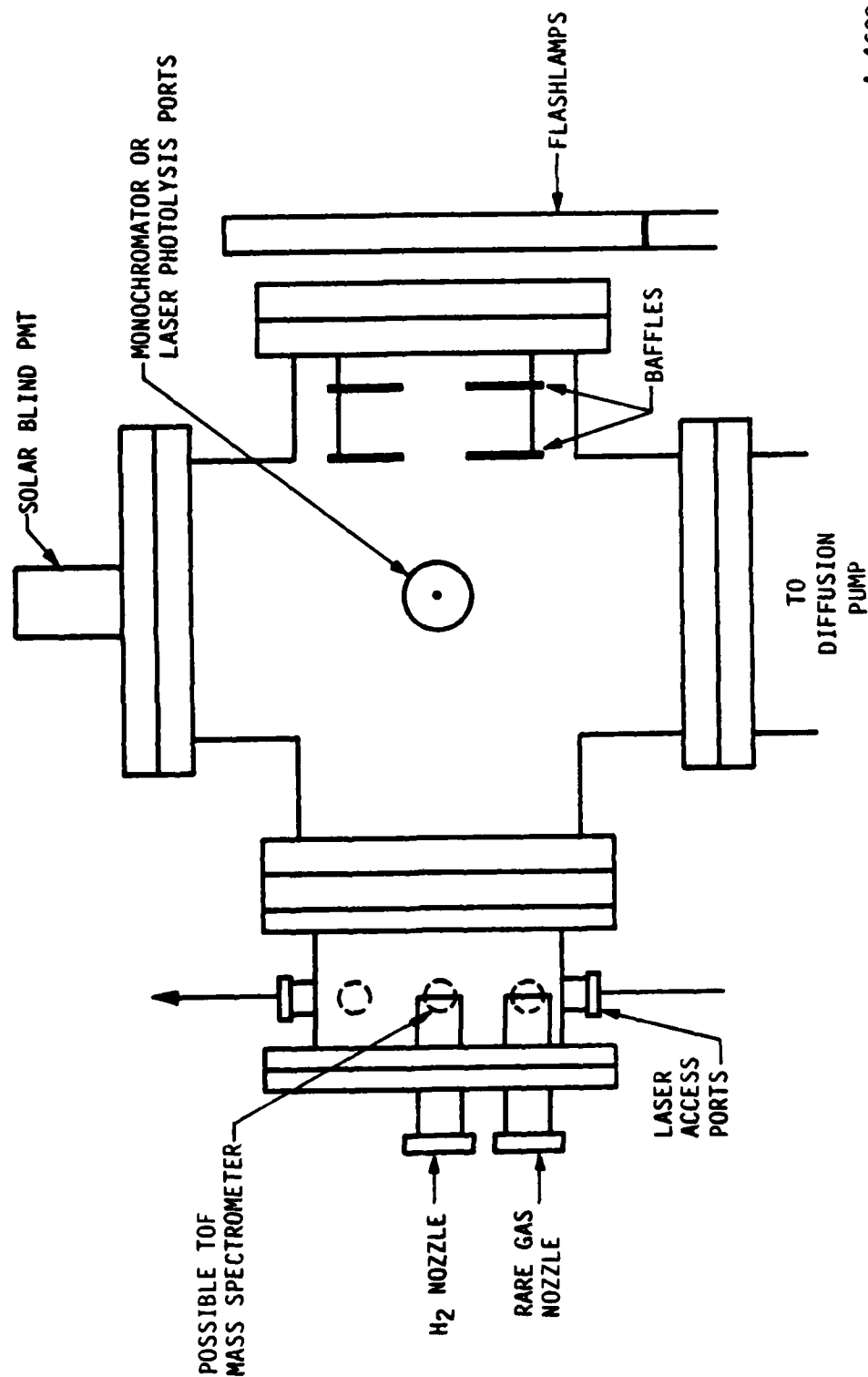


DETECTION OF H_4

- PHOTODISSOCIATION TO FORM $H_2(B)$
 - $\lambda < 500$ nm
 - DETECT $H_2(B)$ EMISSION WITH PMT
 - FLASHLAMP PHOTOLYSIS, $\lambda = 200$ TO 800 nm
 - LASER PHOTOLYSIS, $\lambda = 337$ nm, 266 nm
 - CROSS SECTION UNCERTAIN: 10^{-18} TO 10^{-20} cm^2
 - AT 10^{-20} cm^2 CAN DISSOCIATE 5 TO 10 PERCENT WITH 337 nm
- PHOTODISSOCIATION TO FORM $H_3^+ + H^-$
 - $\lambda < 670$ nm
 - COLLECT TOTAL IONS FORMED WITH ELECTRODES
 - POSSIBLE CONSTRUCTION OF TIME-OF-FLIGHT MASS SPECTROMETER
 - IMPROVED COLLECTION EFFICIENCY FOR IONS INCREASES EXPECTED SIGNAL BY 10^4
- PASSIVE EMISSION
 - QUASI-CONTINUOUS, $\lambda > 153$ nm
 - LOOK WITH PMT/VUV MONOCHROMATOR



EXPERIMENTAL CHAMBER

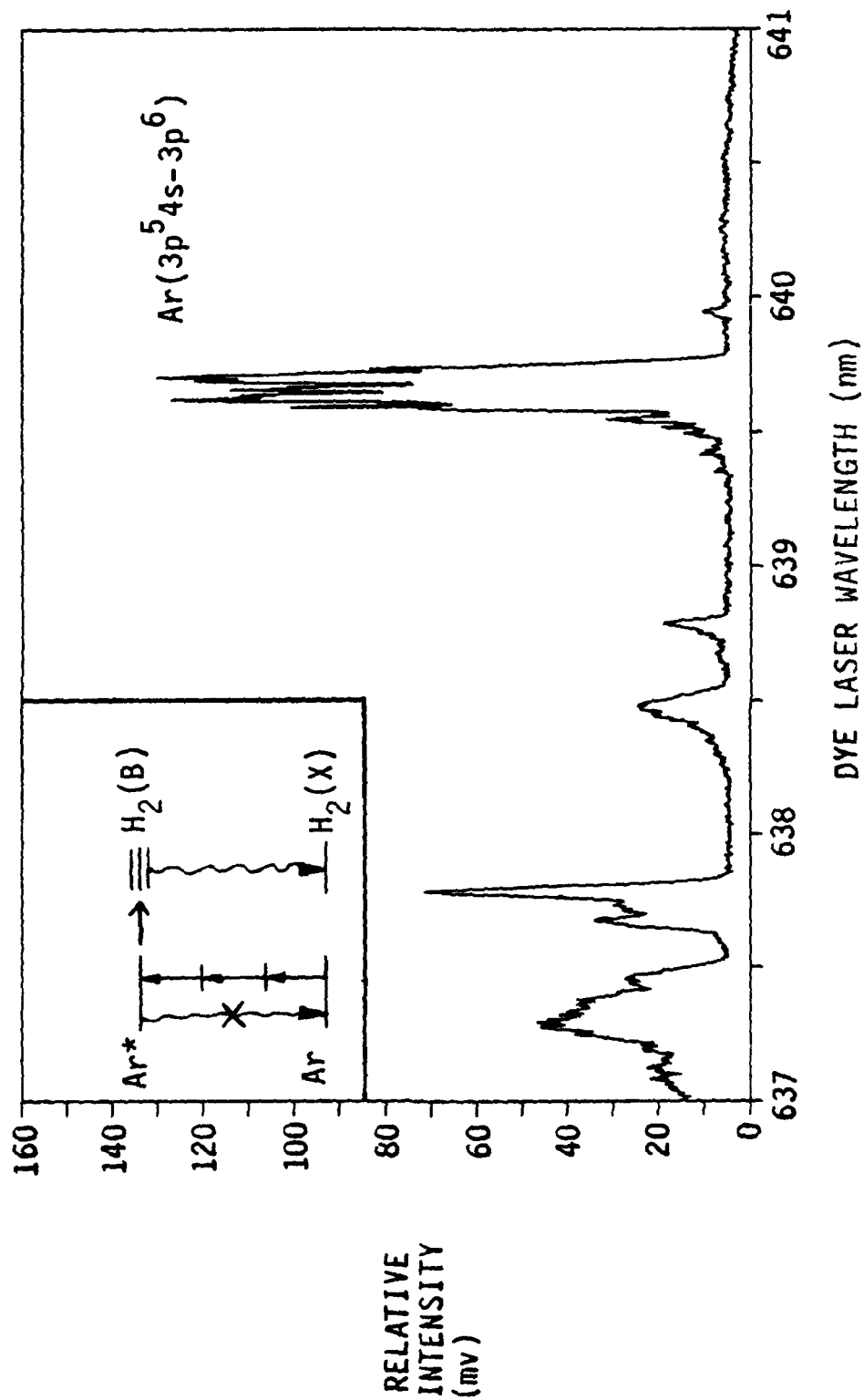


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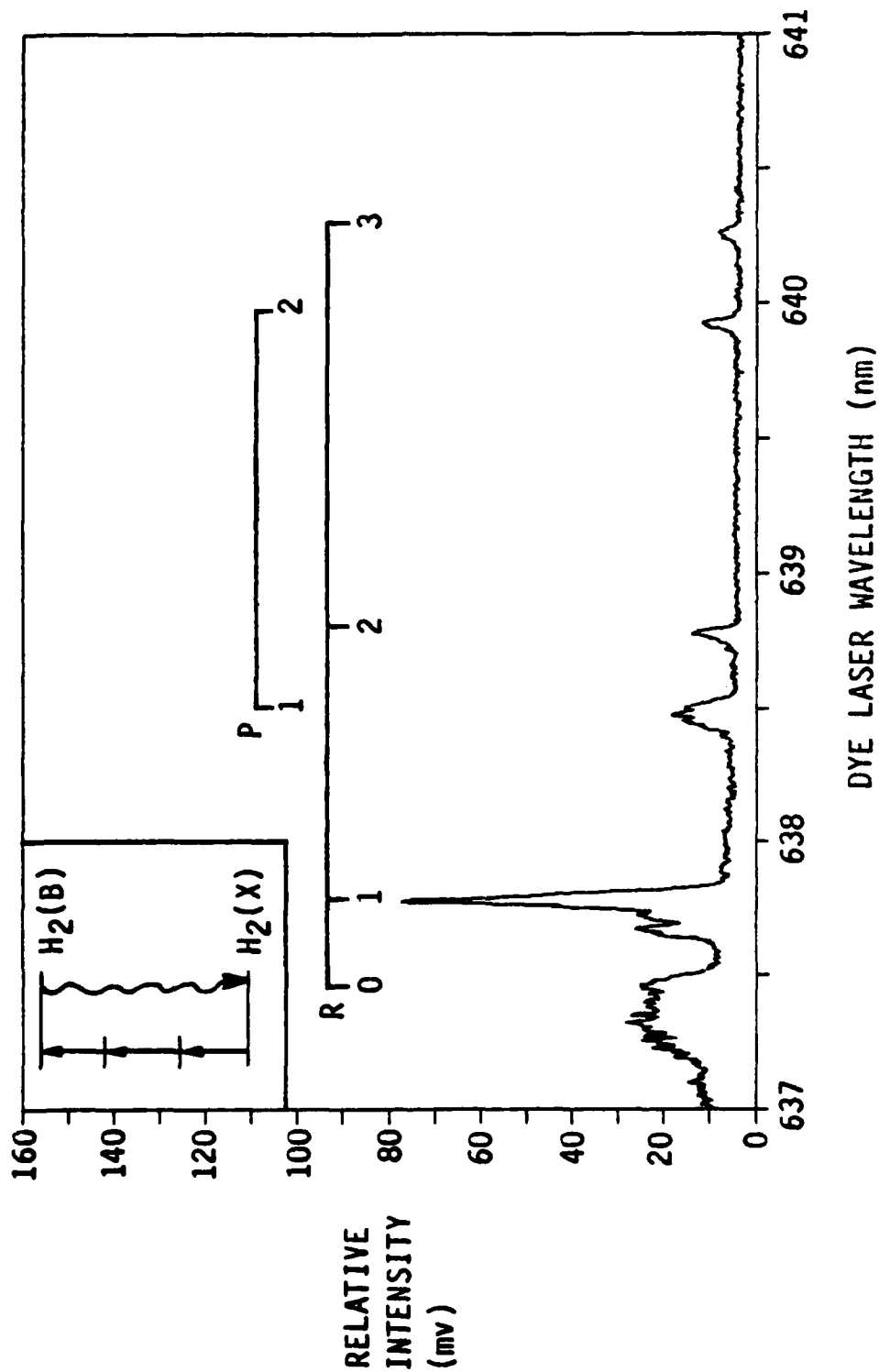
THREE PHOTON H₂ EXCITATION SPECTRUM

$P_{Ar} = 20$ Torr $P_{H_2} = 80$ Torr

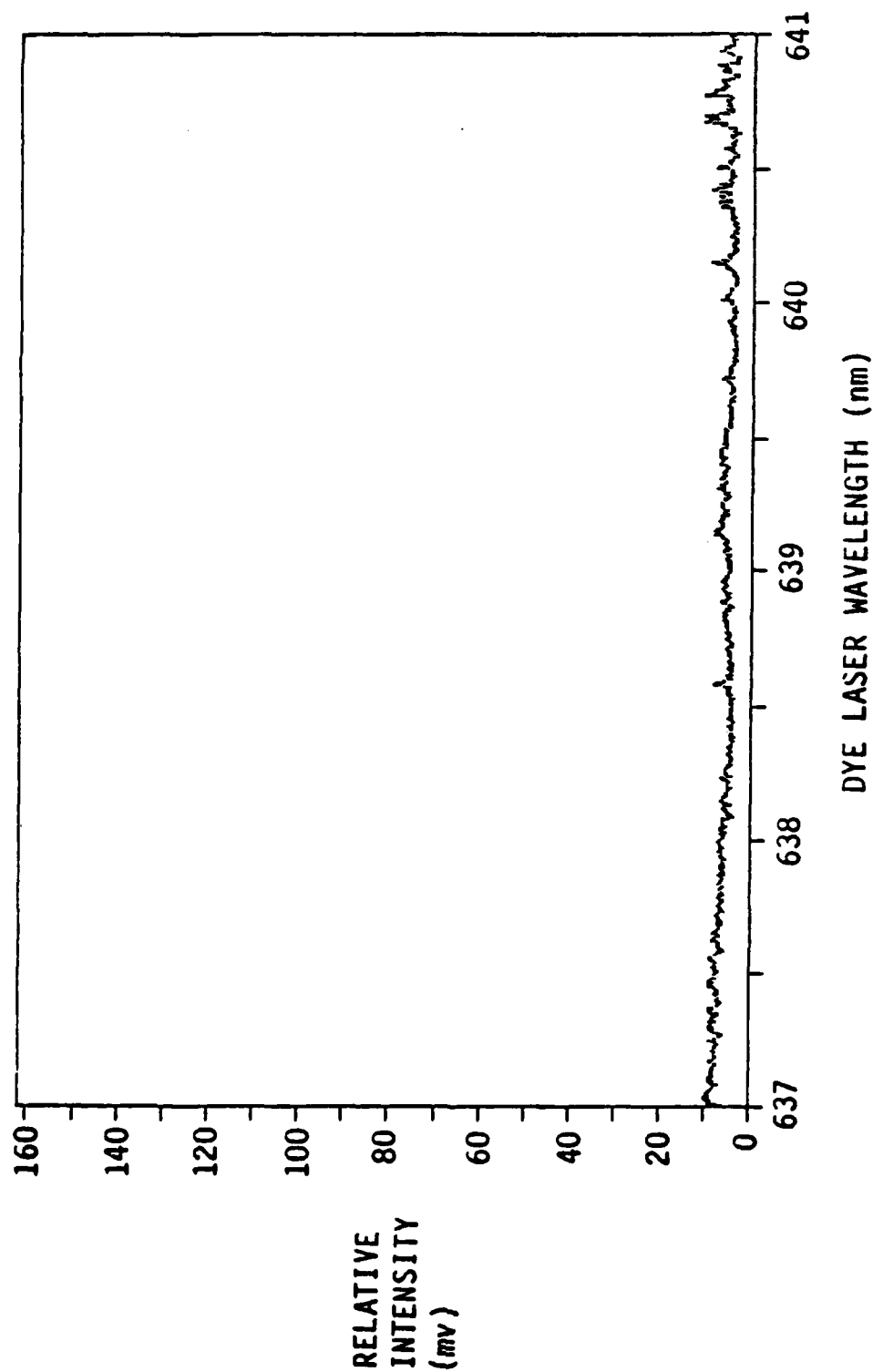


RELATIVE
INTENSITY
(mV)

THREE PHOTON H₂ EXCITATION SPECTRUM H₂(B, v'=3) - H₂(X, v'=0) 80 Torr H₂



Ar EXCITATION SPECTRUM $P_{Ar} = 20$ Torr



SUMMARY

- H₄ TO BE PRODUCED VIA QUENCHING OF H₂(B) BY H₂
 - H₂(B) EXCITED VIA DIRECT EXCITATION AND Ar^{*} ENERGY TRANSFER
 - SUPERSONIC JET EMPLOYED TO ENHANCE FORMATION AND CHARACTERIZATION
- ACTIVE AND PASSIVE DETECTION OF H₄ TO BE EXPLORED
 - PHOTOLYSIS TO PRODUCE H₂(B) OR IONIC PRODUCTS
 - DETECTION OF PASSIVE EMISSION FROM DECOMPOSING EXCIMER
- DEMONSTRATED H₂(B) PRODUCTION VIA THREE-PHOTON EXCITATION AT 319 nm
 - OTHER FEATURES OBSERVED WHICH SCALE NON-LINEARLY WITH H₂ DENSITY
 - COLLISIONAL ENERGY TRANSFER FROM Ar^{*} TO H₂ OBSERVED VIA THREE-PHOTON EXCITATION OF Ar



ABSTRACT

Theoretical Studies of Metastable States of He₂ and H₄

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We have recently developed a series of theoretical methods which are capable of calculating the quenching rates of metastable molecular states due to nuclear and relativistic non-adiabaticity. We currently have the ability to analytically compute the first and second order nuclear non-adiabatic coupling matrix elements, $\langle \Psi_i | d/dR | \Psi_j \rangle$ and $\langle \Psi_i | d^2/dR^2 | \Psi_j \rangle$, as well as to compute quenching rates arising from spin-orbit interactions. The ability to include the effect of spin-spin interactions is being incorporated in our program package and we will report the progress attained in that effort.

These methods have been applied to the studies of H₄ and He₂, and we will report the results of that work. For H₄ we have optimized the structures of the low-lying states at the multi-reference CI level. The lowest state in the pyramidal (C_{3v}) configuration was found to be unstable with respect to symmetry breaking nuclear displacements. The first excited state was of E symmetry in C_{3v} and was found to distort to a C_s minimum with full geometry optimization. Dipole transition moments and non-adiabatic coupling matrix elements were calculated at the minimum of the excited state.

For He₂ we have considered the spin-forbidden radiative transition between the lowest triplet state and the ground state, $a^3\Sigma_u^- \rightarrow X^1\Sigma_g^+$. We have also calculated the spin-orbit coupling matrix elements which are needed to compute the quenching of the lowest triplet atomic state.

Theoretical Studies of Metastable States of He_2 and H_4

Byron Lengsfeld, James Jensen, George
Adams and Cary Chabalowski
US ARMY Ballistic Research Laboratory

David Yarkony
Johns Hopkins University

SPEAKER'S COMMENTS ARE ENCLOSED IN BRACKETS {}

Develop Theoretical Methods

- Characterize Potential Energy Surfaces
 - locate stable points on ground and excited state surfaces
 - compute vibrational frequencies and intensities
- Compute Spin-Forbidden Lifetimes
 - spin-orbit coupling
 - spin-spin coupling
- Compute Nonadiabatic Coupling Terms
 - d/dR terms
 - Rotational couplings

{ Goal is to Develop THE NEEDED THEORETICAL TOOLS
AND .10 Apply THEM TO Promising MOLECULAR SYSTEMS }

Theoretical Methods Used to Characterize Potential Energy Surfaces

Perturbation Theory
Coupled-Cluster Wavefunction
Multi-Reference CI *1,000,000 CSFs*

MCSCF *10,000 CSFs*
SCF *1 CSFs*

Σ Current Capabilities of Theoretical Methods }

{Multi-Configuration description is needed for
excited states and for systems where resonance
is important}

See p. 5792 of J Am Chem Soc, 108(19), 1986.

TABLE III. COMPARISON OF EXPERIMENTAL AND THEORETICAL FREQUENCIES, TOTAL ENERGIES, AND GEOMETRIES FOR H₂CO
(Frequencies in cm⁻¹)

MODE	EXP.	DZP SCF	BAG SCF	BAG DMC 6/6	DZP SDMC 6/6	DZP DMC 6/6	DZP DMC 6/12	DZP CI	dTZP DMC 6/6	DZP+dSPD DMC 6/6
$\nu_6(B_1)$	1190	1335	1287	1170	1221	1222	1223	1272	1236	1215
$\nu_5(B_2)$	1282	1367	1319	1244	1291	1292	1291	1305	1295	1282
$\nu_3(A_1)$	1561	1656	1604	1506	1560	1560	1560	1596	1566	1547
$\nu_2(A_1)$	1767	2007	1861	1712	1849	1850	1870	1868	1847	1847
$\nu_1(A_1)$	2940	3148	3081	2897	2940	2944	2957	3074	2911	2922
$\nu_4(B_2)$	3016	3226	3178	2979	3002	3007	3023	3173	2972	2985

Total* Energy (Hartrees) --- -0.895328 -1.031216 -1.063136 -1.195568 -1.070912
-0.852032 -1.063553 -1.133902 -1.074239

Bond Angle (degrees) 116.5 116.2 117.2 117.2 115.85 115.9 116.4 116.3 116.0 116.3
Bond Length CO 1.203 1.189 1.209 1.236 1.213 1.213 1.210 1.212 1.207 1.210
(A) 1.099 1.094 1.091 1.110 1.115 1.115 1.114 1.095 1.112 1.114

*Energies needed to be added to -113.0.

*Finite-Difference Results (step length of .001 bohr)

{ EXAMPLE OF RECENT WORK EMPLOYING
DERIVATIVE TECHNIQUES }

TABLE II. THEORETICAL INTENSITIES COMPUTED WITH HYBRID BASIS SETS⁺

(Intensity in KM/MOLE)

MODE	EXP	BAG/EXP		BAG/DZP		BAG/dTZP ^Δ		BAG/DZP		dTZP+d [†] /dTZP	
		SCF		DHC	6/6	DHC	6/6	CI		DHC	6/6
ν ₆	6.5	6.2		5.5		5.3		8.2		4.1	
ν ₅	9.9	18.9		12.4		12.9		11.0		14.4	
ν ₃	11.	33.2		10.9		7.4		13.8		11.6	
ν ₂	74.	107.9		81.2		85.7		72.		107.8	
ν ₁	75.	72.7		59.4		62.8		53.7		68.1	
ν ₄	87.	112.1		87.1		83.3		80.5		96.6	

⁺ The notation XXX/YYY indicates that the dipole derivatives were computed with basis XXX at the geometry obtained with basis YYY and using the YYY normal modes.

^Δ dTZP = Bacskey sp basis + tight set of polarization functions.

[†] dTZP basis + diffuse polarization functions.

Spin-Orbit interactions

{Sum over states is avoided by solving a large set of linear equations (eqn 2.5a of reference). This means large, direct-CI wavefunctions can be employed and the slow convergence of a sum over states perturbation expansion is avoided. See Yarkony, J Chem Phys, 85, 7261(1986)}

{Same approach is being developed for spin-spin interaction}

-----NEXT SLIDE-----

{We can exploit work on derivatives of CI wavefunctions to compute non-adiabatic matrix elements}

See J Chem Phys, 81(10), 4549(1984).

-----NEXT SLIDE-----

See equation 2.8 of J Chem Phys, 81(10), 4549(1984)

{Two terms need to be evaluated}

See equation 2.12a and 2.12b of J Chem Phys, 81(10), 4549(1984)

{Trace of a one-particle density matrix with a half-derivative overlap integral}

Non-Adiabatic Coupling

Born-Oppenheimer Approximation

Matrix Elements

$$\langle \psi_i | d/dR | \psi_j \rangle$$

$$\langle \psi_i | L_T | \psi_j \rangle$$

$$\langle \psi_i | d^2/dR^2 | \psi_j \rangle$$

ROTATIONAL
COUPLING

Derivative Methods

CI gradient

See equation 2.13b of J Chem Phys, 81(10), 4549(1984)

{CI gradient evaluated with a transition density matrix}

-----NEXT SLIDE-----

See Figure 1 of Ginter, M.L. and Battino, R., 4470.

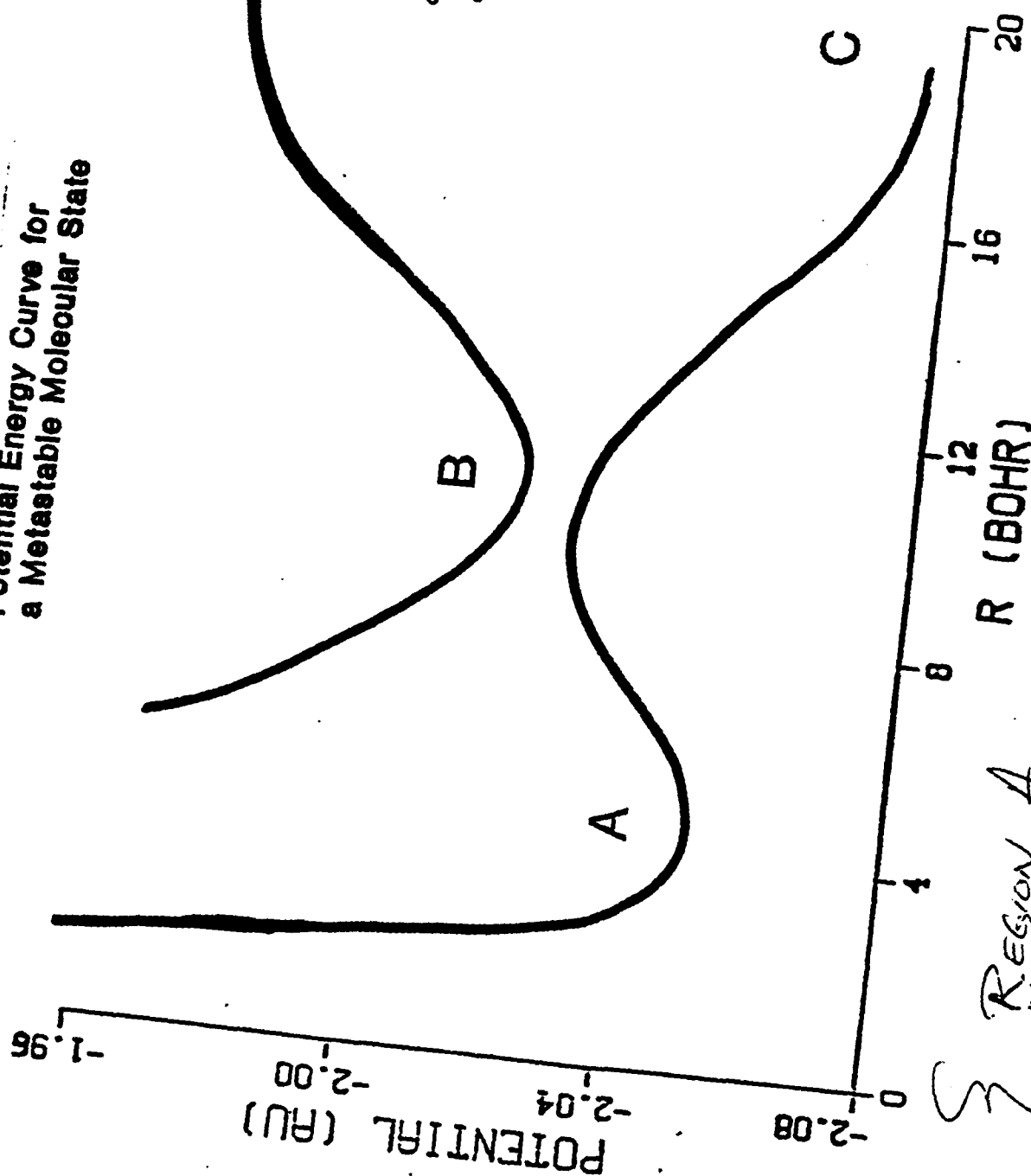
{A large number of curve crossings must be considered. Relativistic interactions can result in avoided crossings.}

Theoretical Studies of H_4

- Characterize both stable points
optimized structures
- Compute Vibrational Frequencies
Multi-Reference CI Level
- Estimate the Radiative Lifetime
of the Excited State
- Compute Nonadiabatic Coupling Terms

Figure 4

Potential Energy Curve for
a Metastable Molecular State



{ EXCITED STATE (B)
CAN RADIATE IN H_2
via a dipole-
allowed mechanism }

REGION A IS OF INTEREST FOR ENERGY STORAGE IN H_2 .
A₁ FOUND TO BE UNSTABLE IN REGION A AT SCF AND MOCF
LEVELS IN PRELIMINARY CALCULATIONS?

Theoretical Studies of He₂

Input Parameters to Liquid Simulation

- Stability of the ³S ^{STATE} ~~excited~~ of He
- Spin-Orbit Lifetime ³Σ_u⁺ state of He₂
- Spin-Spin Coupling
- Nonadiabatic Terms
- Characterize states of He₂, He₃, He₄ etc

Lifetime of the $^3\Sigma_u^+$ State of He_2

spin-orbit operator

$$\frac{1}{2c^2} \sum_i \sum_k \frac{z(k) \mathbf{r}_{ik} \times \mathbf{p}_i \cdot \mathbf{S}_{i+1} \hbar^{300}}{r_{ik}^3}$$

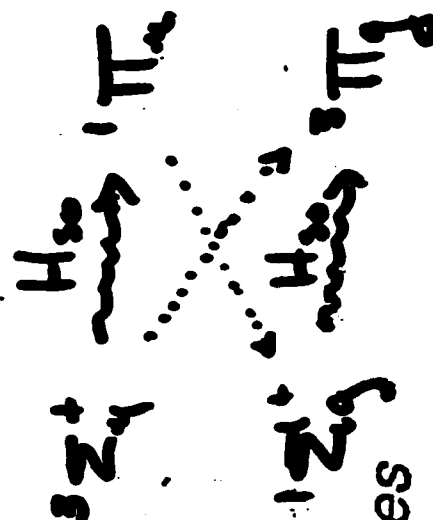
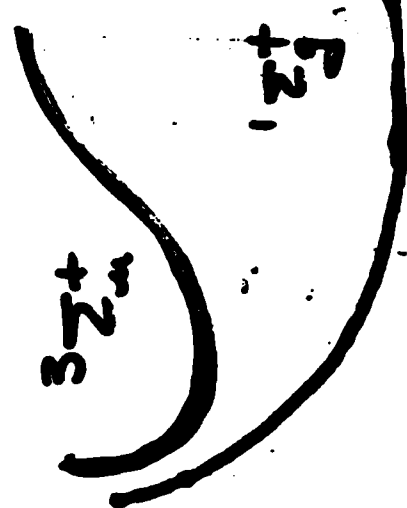
dipole allowed transition

$$\langle ^1\Pi_u | y | ^1\Sigma_g^+ \rangle$$

$$\langle ^3\Sigma_u^+ | y | ^3\Pi_g \rangle$$

think in terms of relativistic states

$$\langle \psi_{^1\Sigma_g^+}^0 + \psi_{^3\Pi_g}^1 | y | \psi_{^3\Sigma_u^+}^0 + \psi_{^1\Pi_u}^1 \rangle$$



Abstract for
The First Annual High Energy Density Matter (HEDM) Conference
May 12-13, 1987
Crystal City, VA

The Influence of Condensed Phase on Metastability

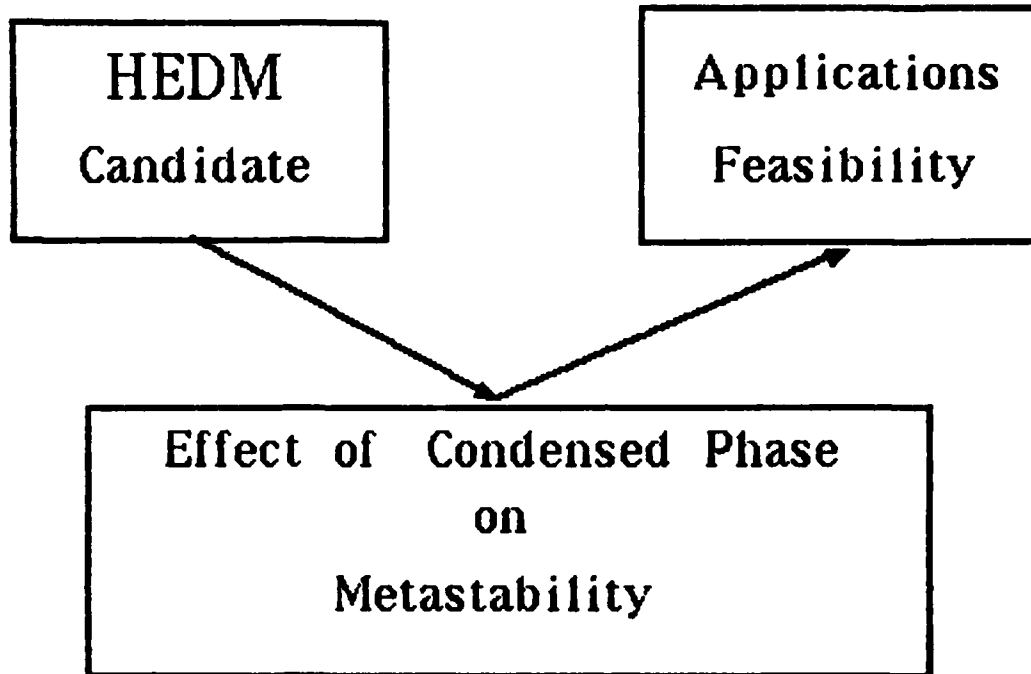
by

P. K. Swaminathan*, C. S. Murthy, B. C. Garrett, and M. J. Redmon
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9560 Pennsylvania Avenue #106
Upper Marlboro, MD 20772

Condensed phase influence on HEDM candidates plays a critical role in determining the lifetimes and storage conditions, thereby ultimately influencing their practical usefulness. We have developed a comprehensive theoretical methodology involving quantum chemistry input, modern computer simulation techniques (such as Monte Carlo, Molecular Dynamics, and Generalized Langevin Dynamics), and semiclassical eikonal description of electronic inelasticity to investigate various aspects of the underlying microscopic energy transfer mechanisms.

We will show illustrative results obtained with the new methodology for the well known examples of liquid Helium metastables, so far employed in this research as convenient prototypes. The experience gained in modeling metastability in these cases has laid the foundation for future studies on other potential HEDM candidates.

Program Plan



Our Role:

**Develop Methods for Elucidation of
Quenching Mechanisms in Gas
and
Condensed Phases**

? HEDM ?

Scenario:

HEDM's involve energetic species, usually
in an ELECTRONICALLY EXCITED state

Therefore, the chemistry and quenching
mechanisms involve

ELECTRONICALLY NONADIABATIC

Collision Dynamics

Condensed Phase materials
low molecular weight inert species

Temporary Prototypes:

Helium Metastables $\text{He}^*(^3\text{S})$ and

He_2^* (a - state) in Helium Liquid

Technical Approaches

Gas-Phase

Self-Consistent Eikonal Method (SCEM)

**Electronic amplitudes coupled to
Nuclear Trajectories via an Ehrenfest
Effective Potential**

**A Self-Consistent Semiclassical
Description practical for polyatomics**

Condensed Phase

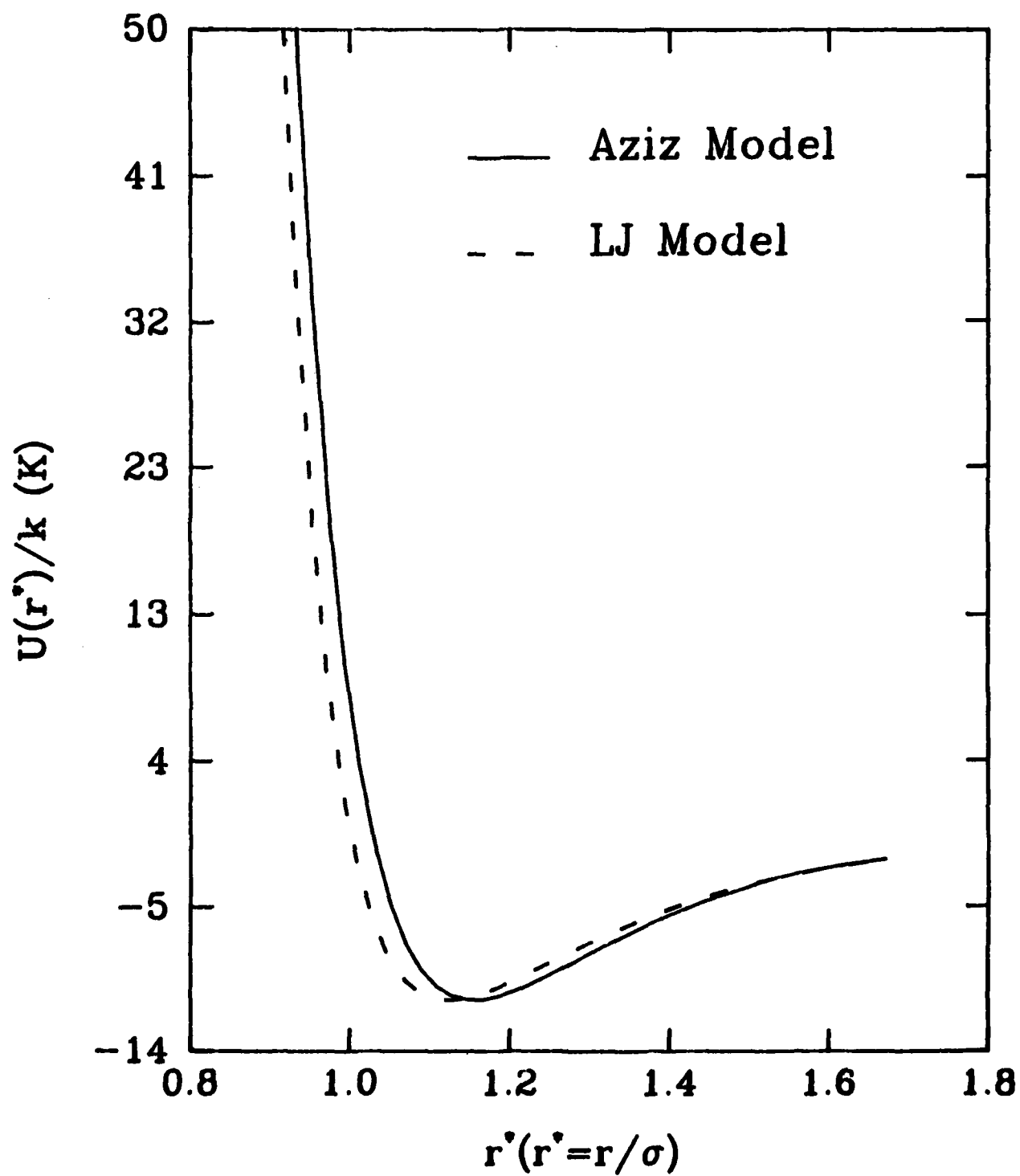
**Computer Experiments: Monte Carlo,
Molecular Dynamics**

Few- body Models :

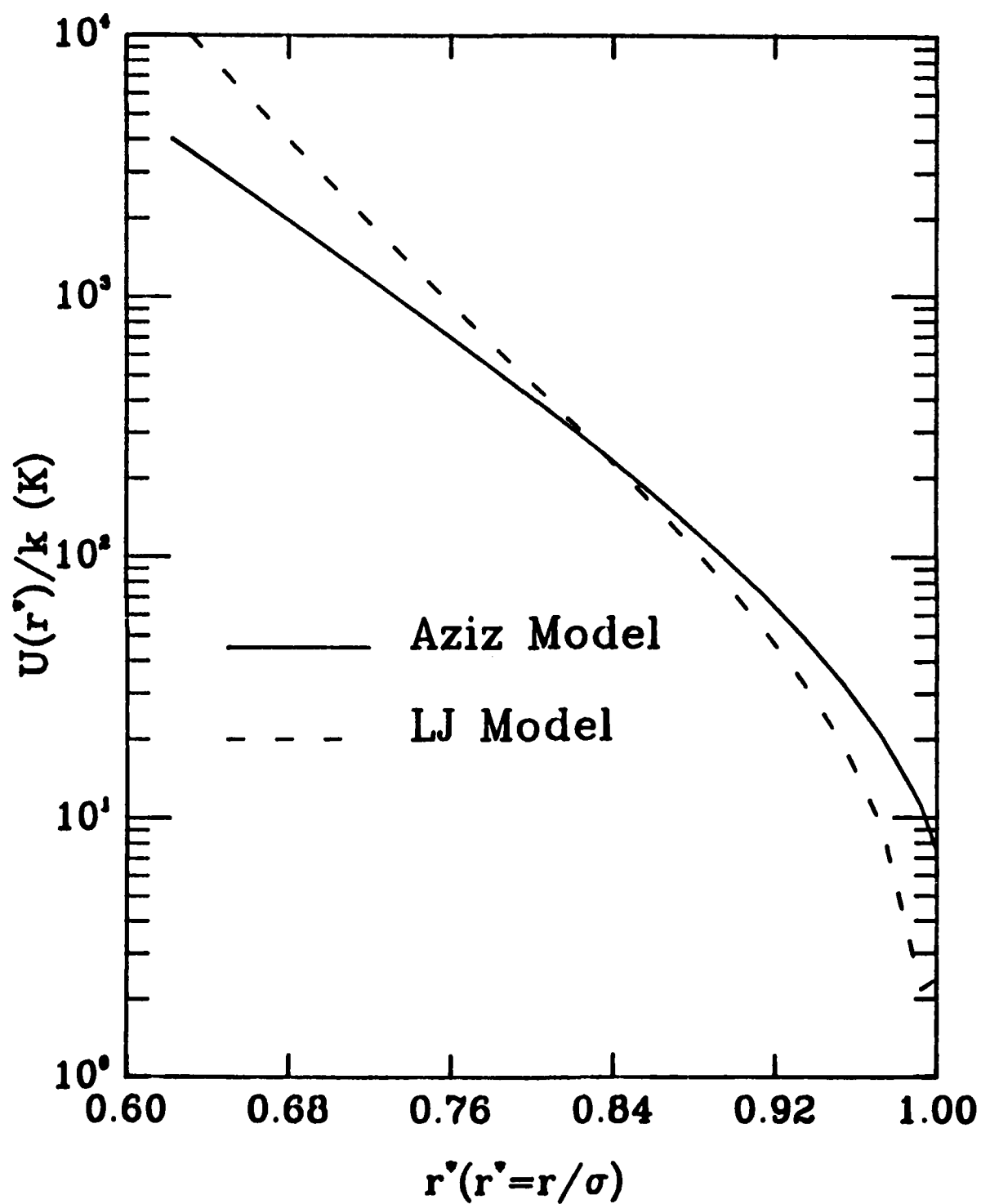
**SCEM + Generalized Langevin Equation (GLE)
based STOCHASTIC MODELS**

**System + Heatbath Decomposition with
one-time heatbath parameterization via
computer experiments**

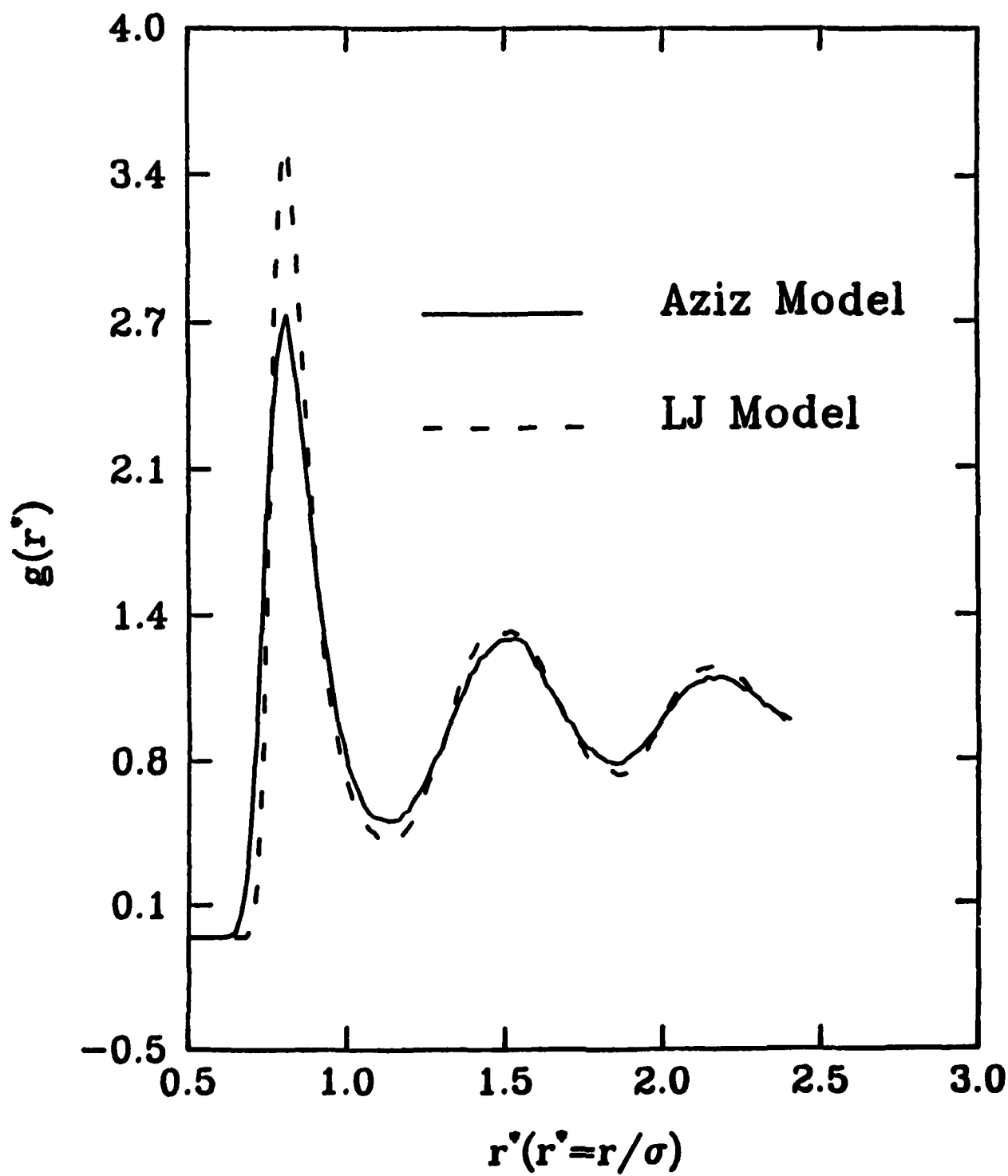
He-He Effective Pair Potentials



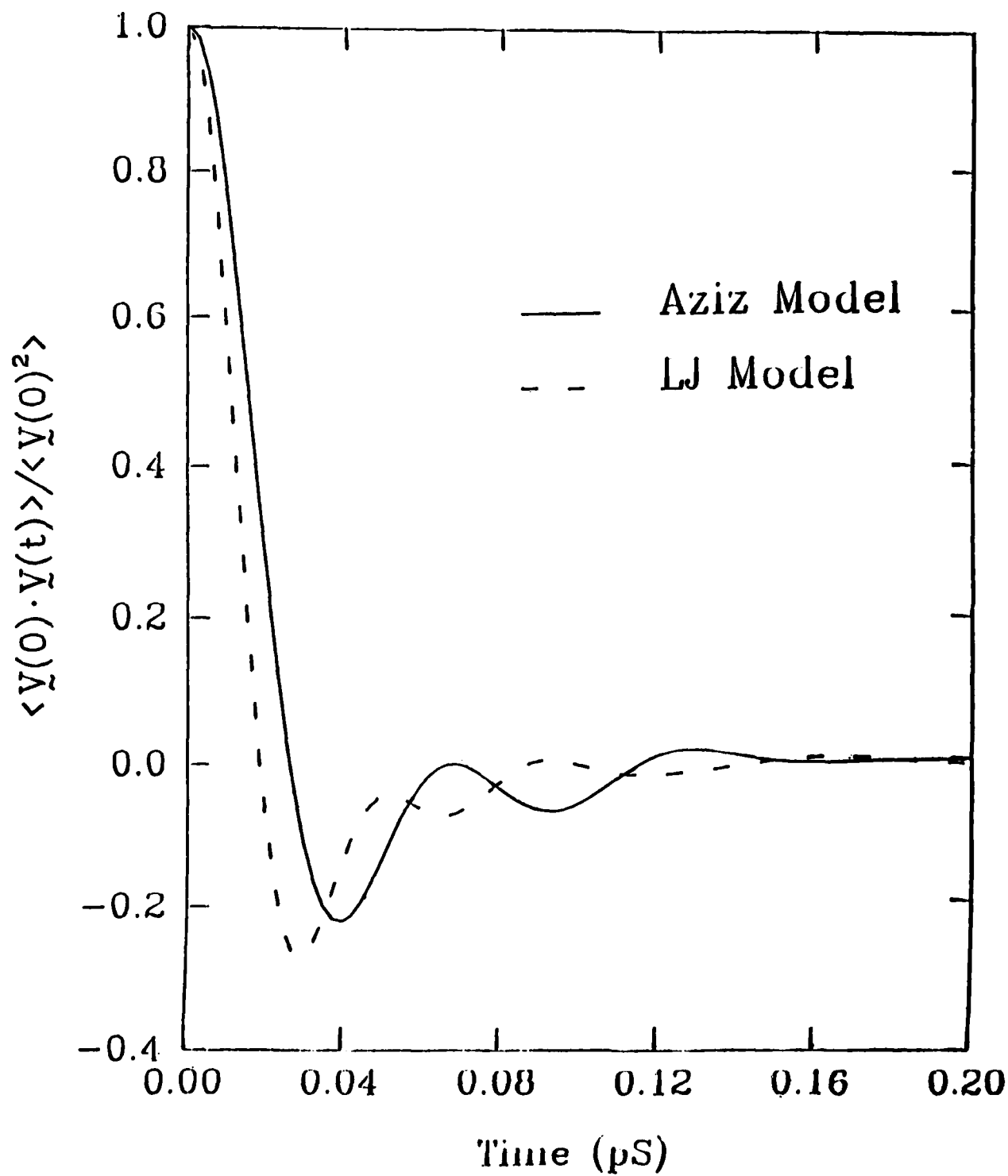
He-He Short-Range Interactions



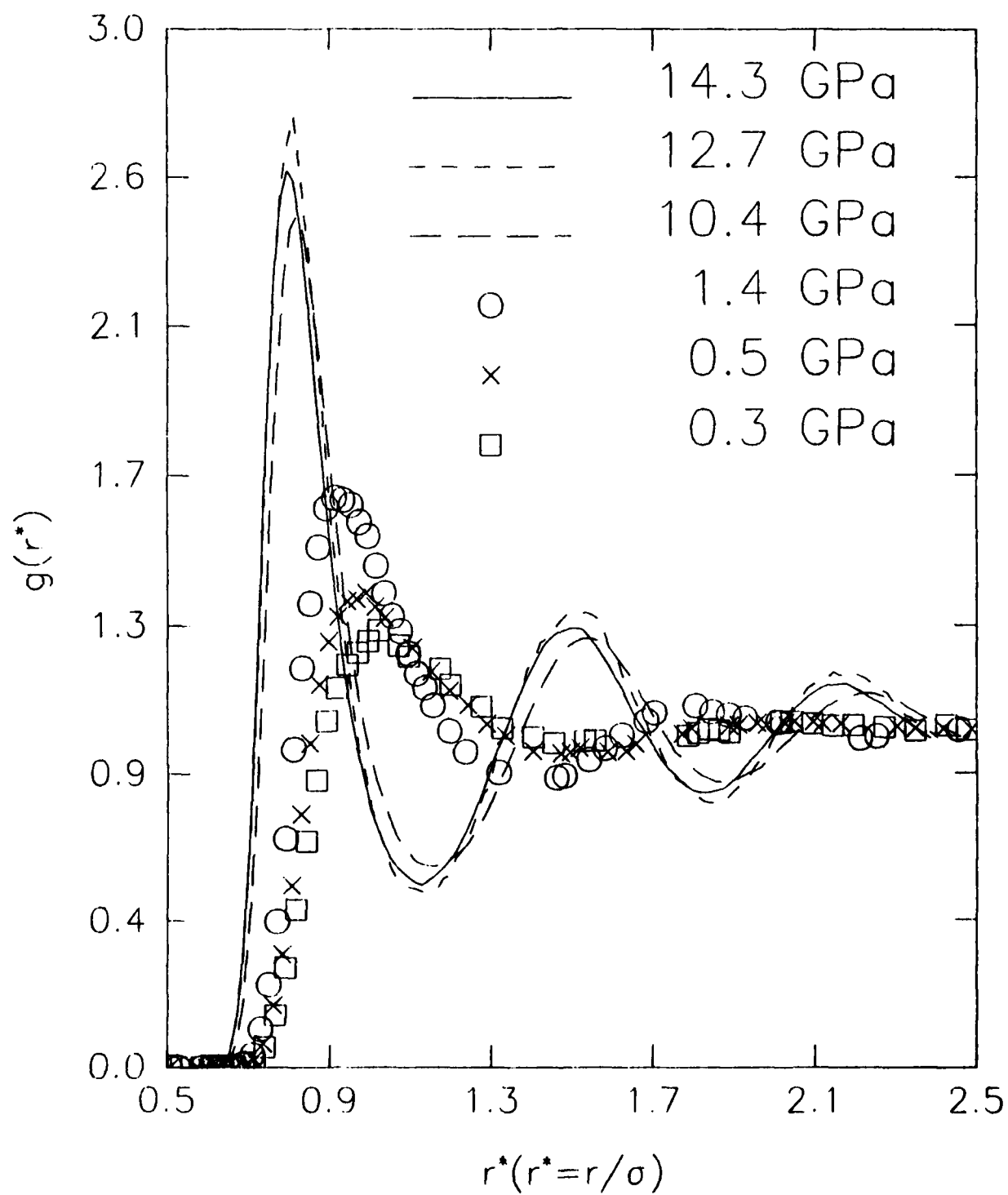
Liquid Structures of Model Helium



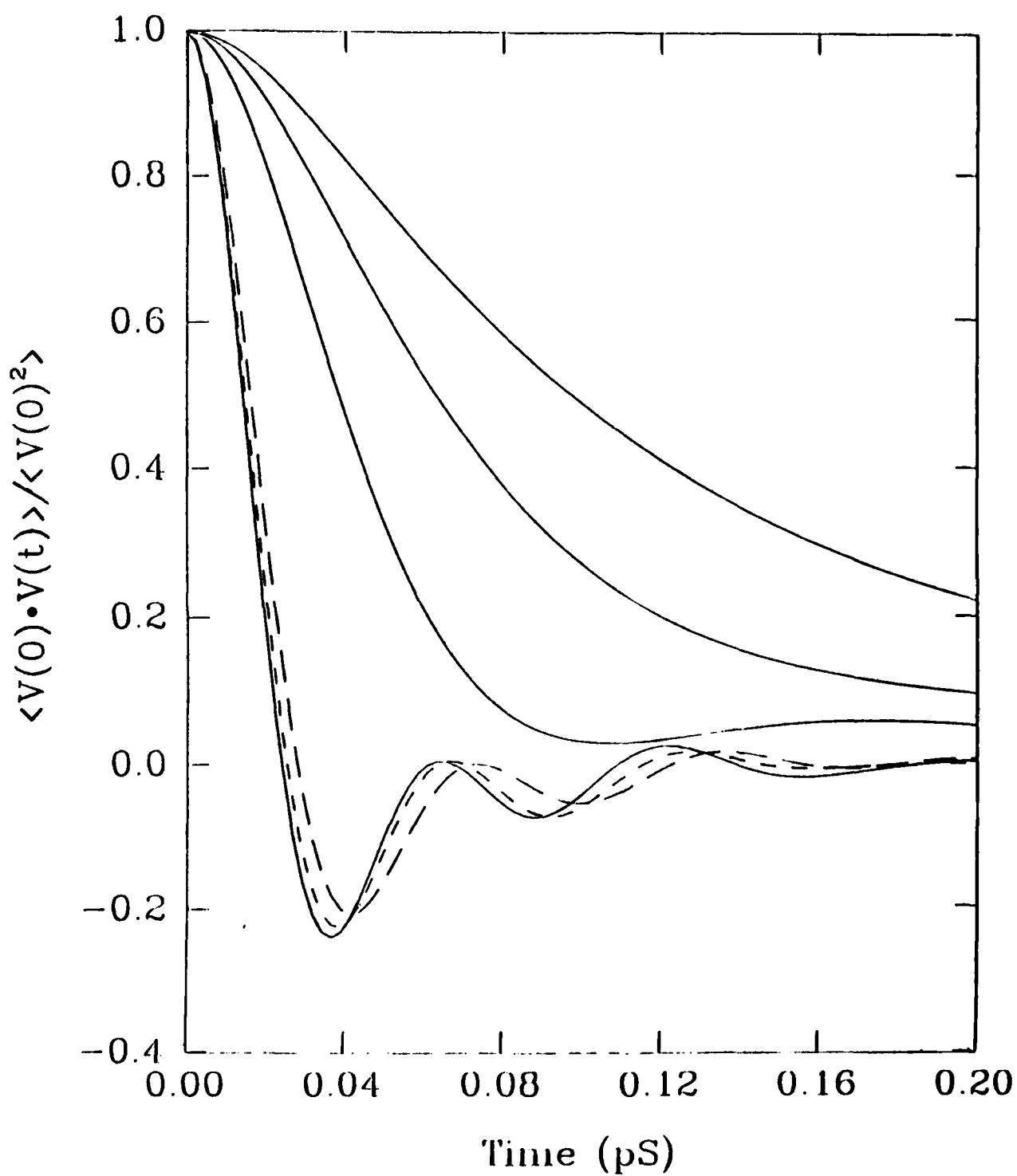
Liquid Dynamics of Model Helium



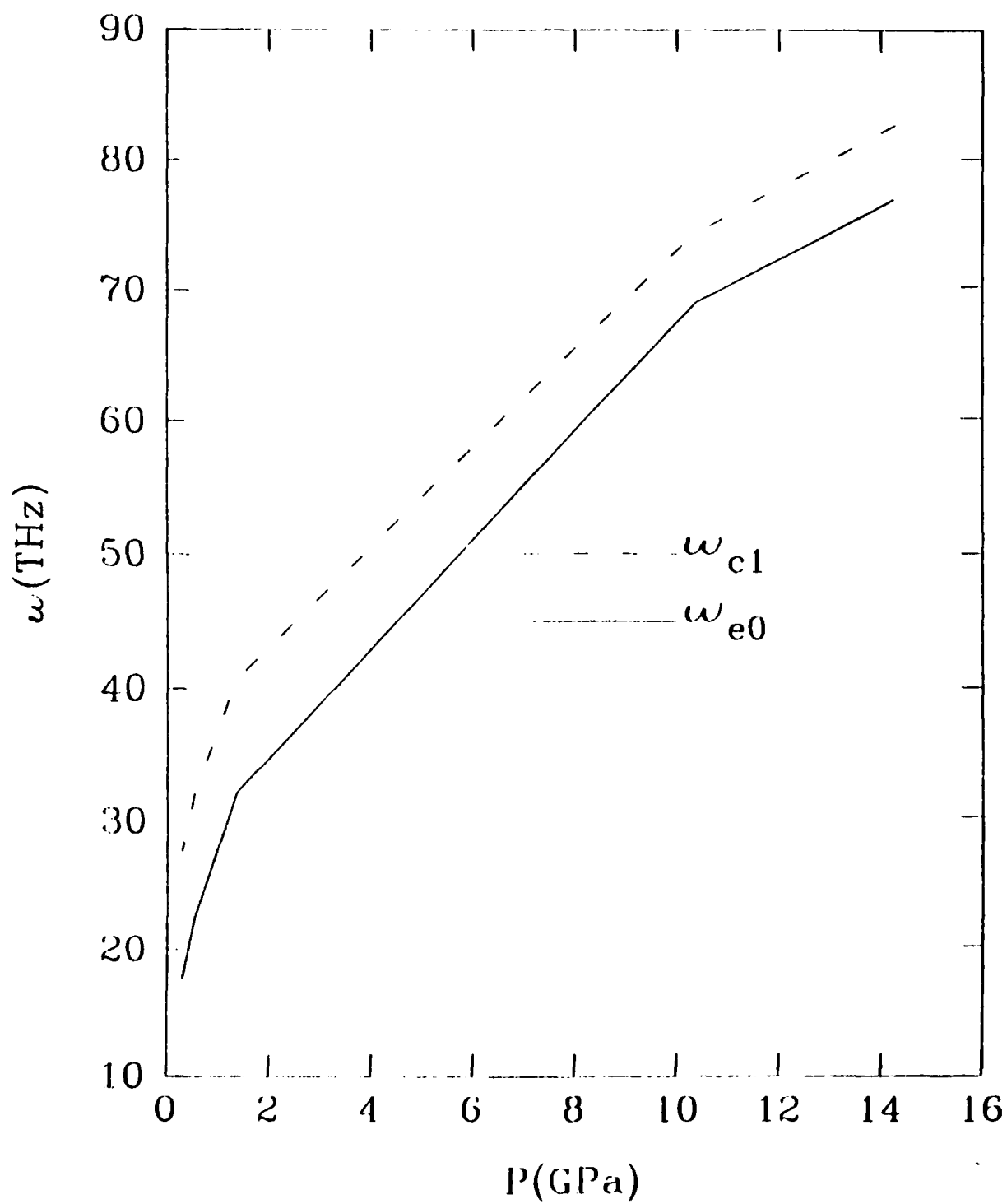
Fluid Structures of Model Helium



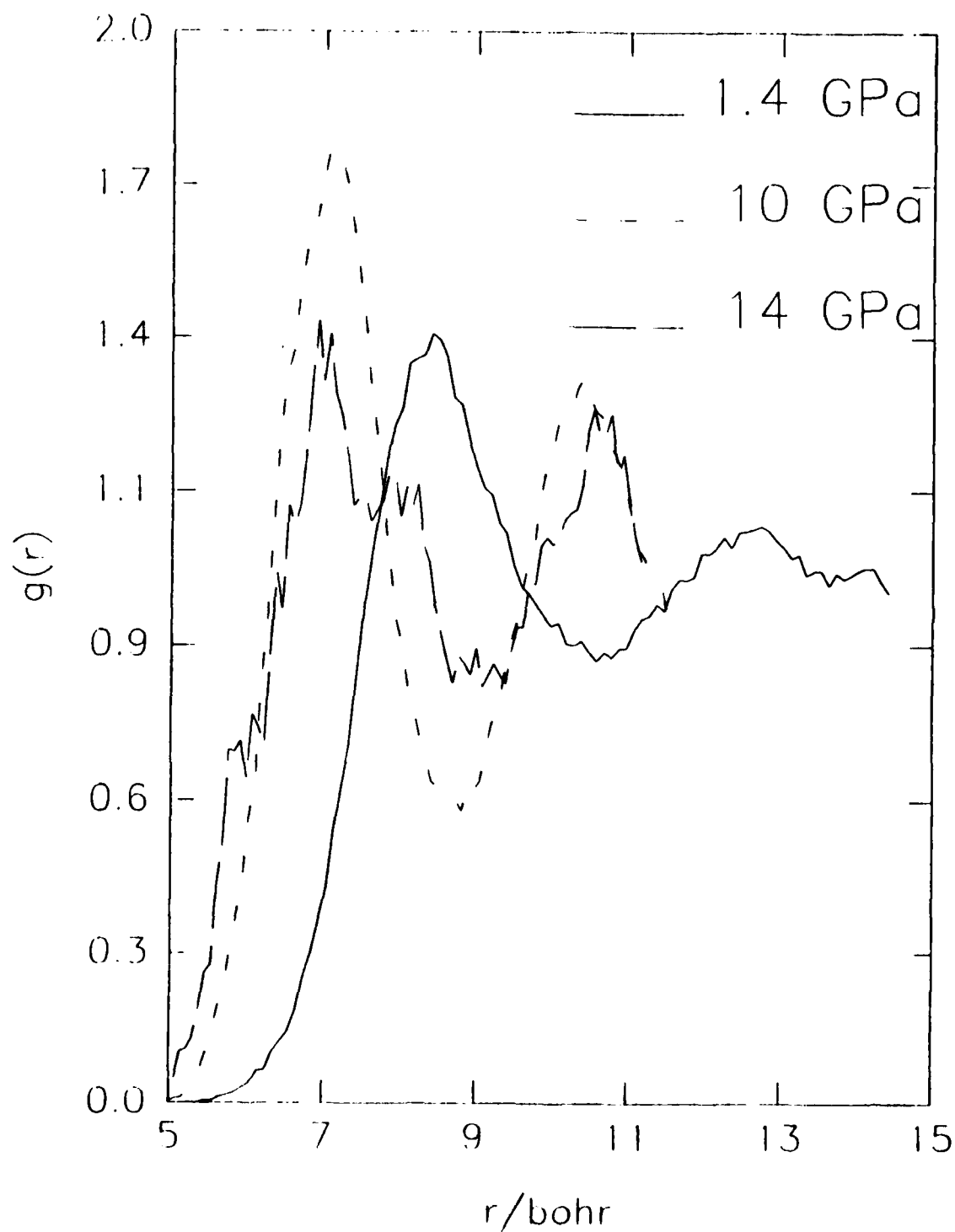
Fluid Dynamics of Model Helium



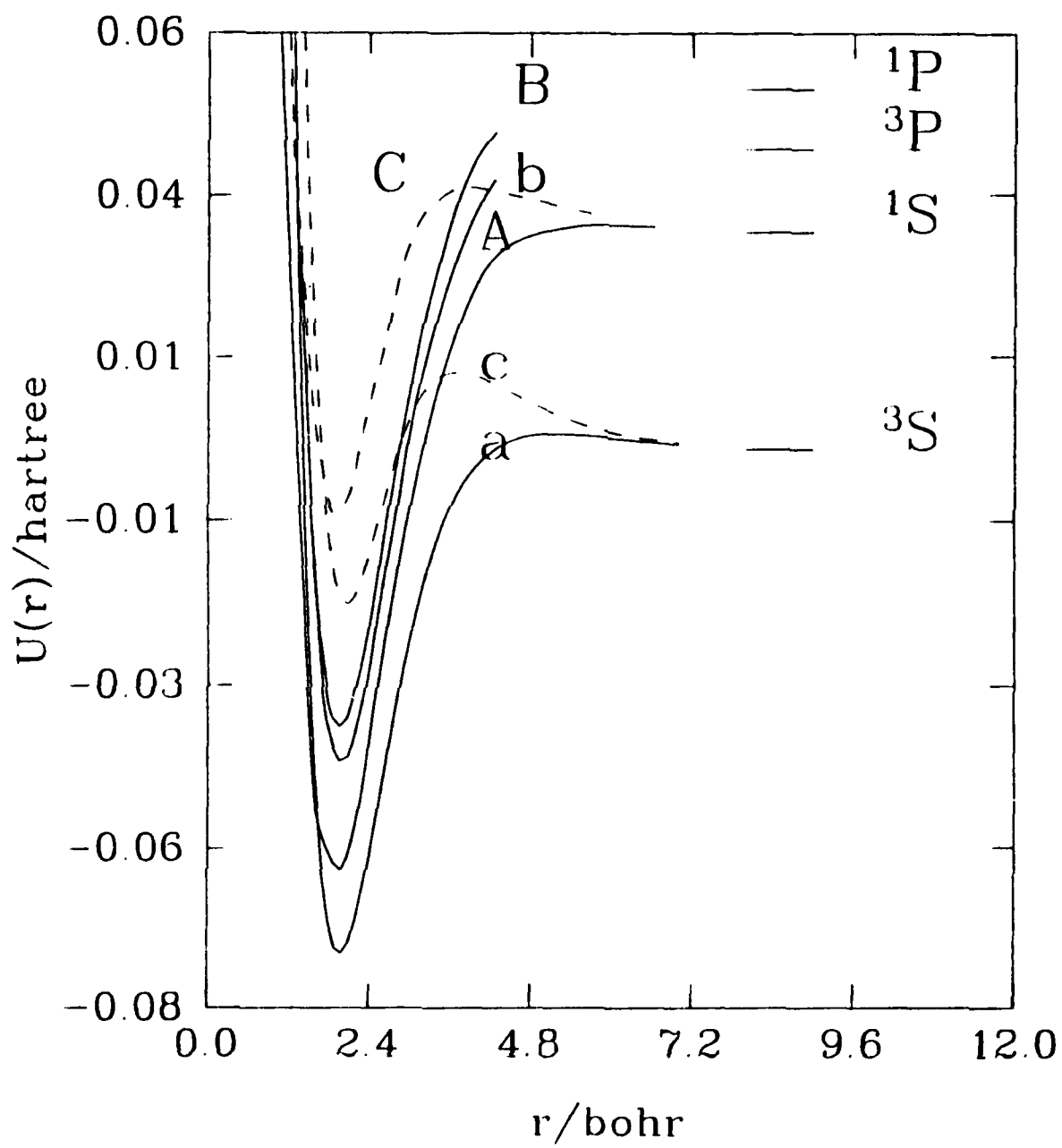
GLE parameters



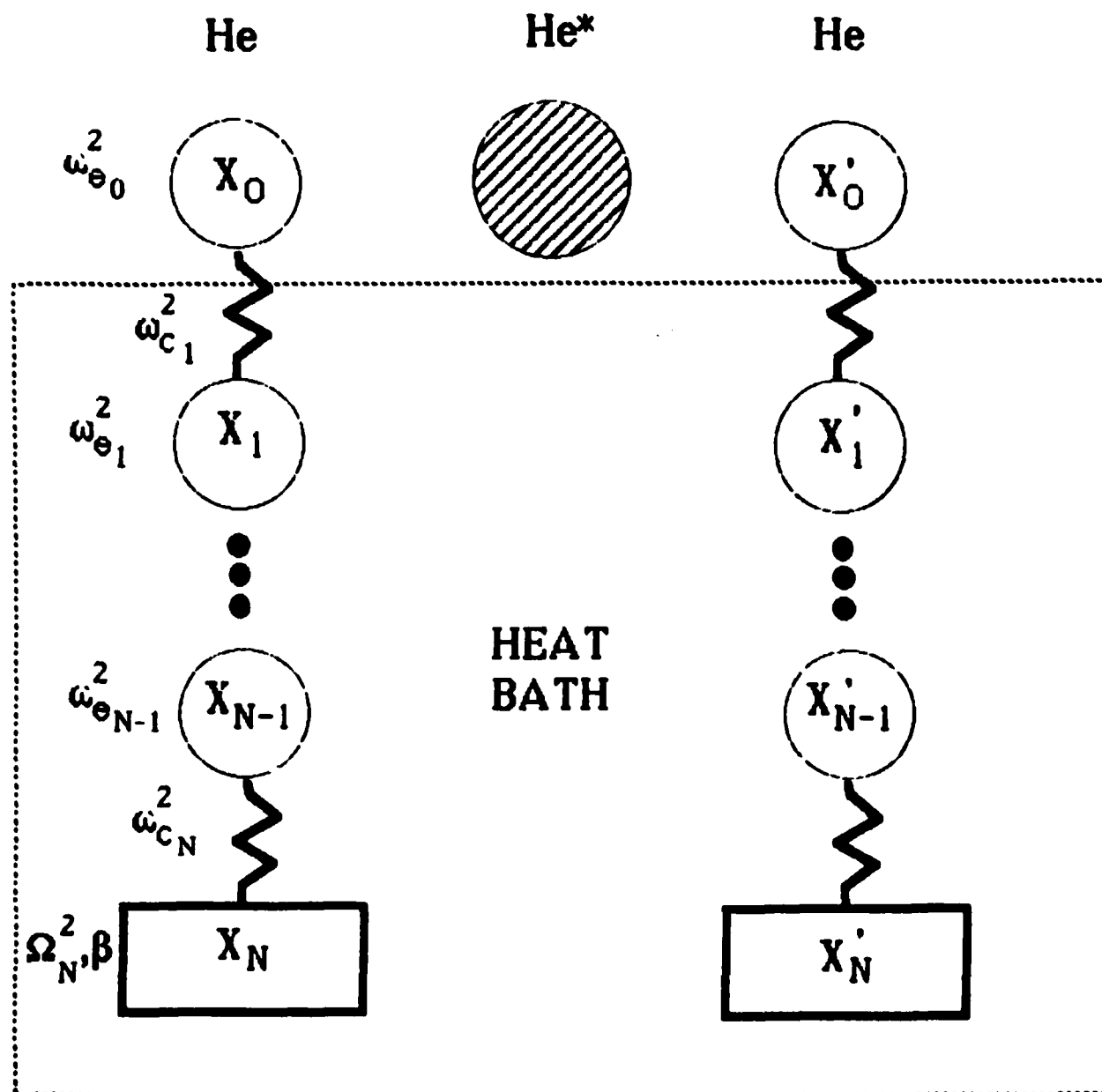
He^{*}-He RDF for a-state



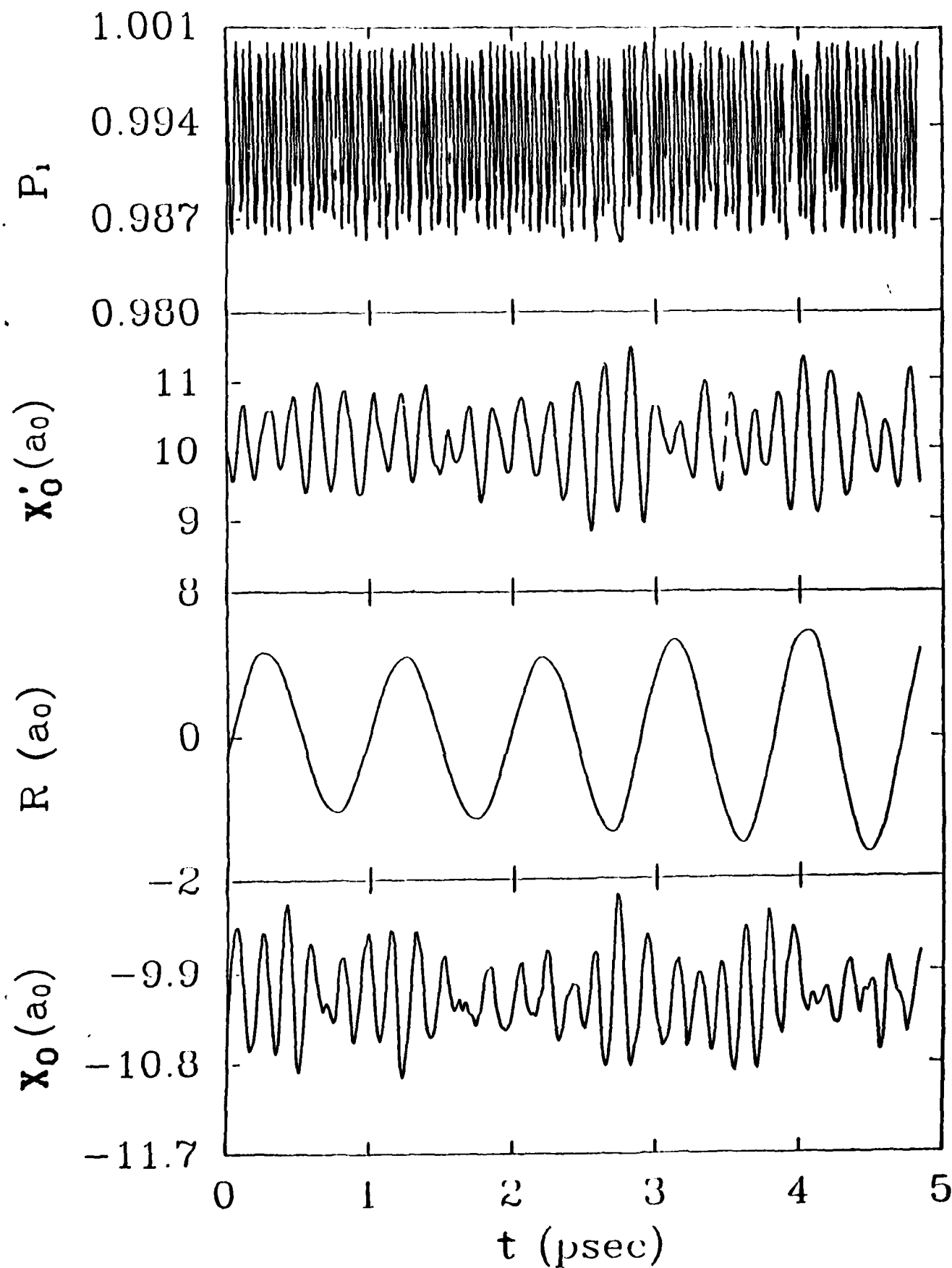
He₂^{*} Interaction Potentials



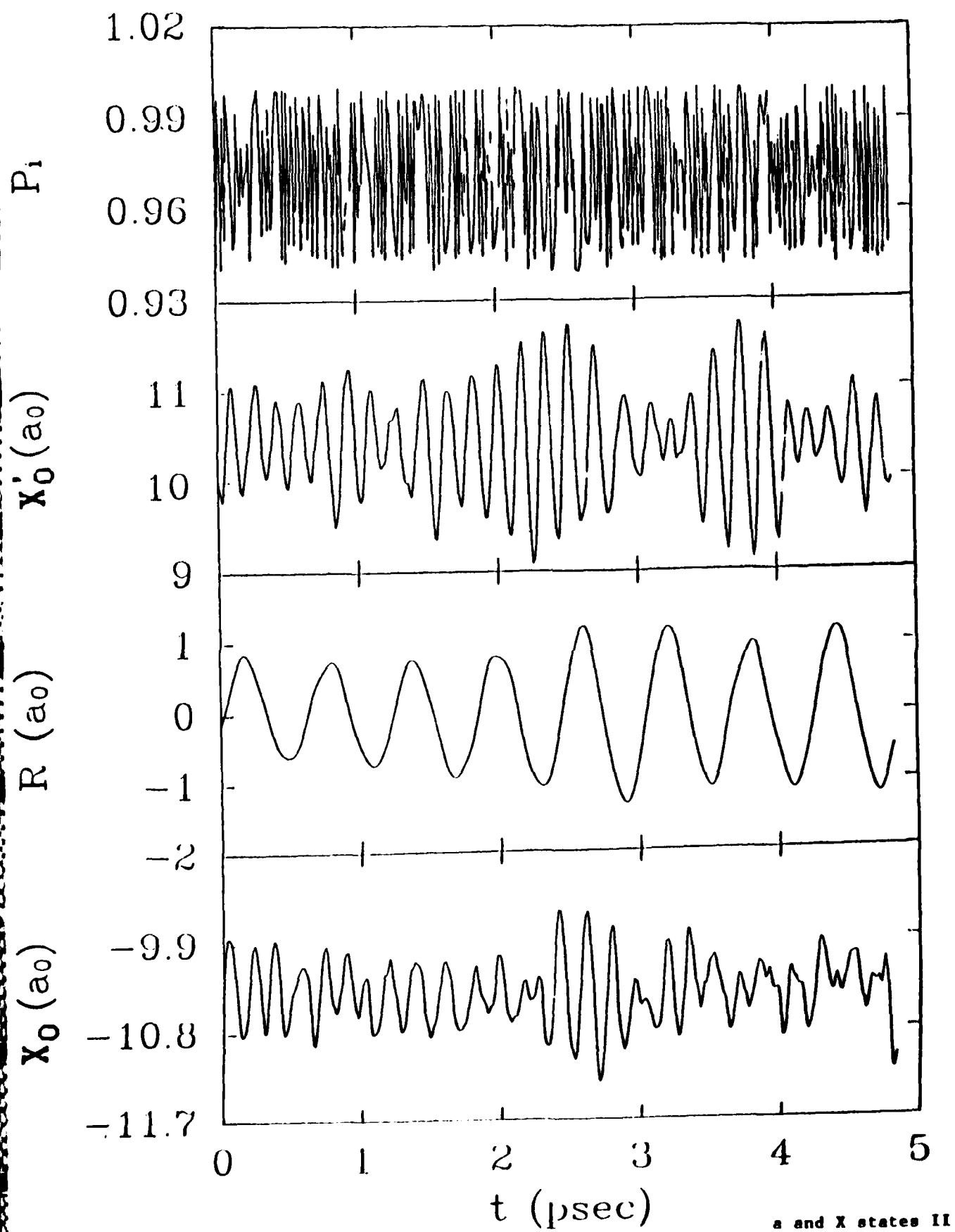
STOCHASTIC TREATMENT OF HELIUM BUBBLE



Helium bubble with a-state and X-state He_2^* using arbitrary coupling.
 Figures show effect of increasing the coupling by a factor of two.



a & X states I



OPTIMIZED TRIAL FUNCTIONS FOR QUANTUM MONTE CARLO STUDY OF H_4^*

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In recent years the fixed-node quantum Monte Carlo method (FNQMC) has been successfully applied to the calculation of electronic energies of small molecules. The attractive feature of this method is that with a modest basis set and often a single-Slater determinant one typically recovers over 90% of the correlation energy.

Because the simulation is dominated by a trial function that fixes the nodal positions, a good trial function is essential in order to obtain an accurate result. It is often chosen to be an *ab initio* approximate Hartree-Fock wavefunction in which case the many-electron nodes are established without consideration of electron correlation. Introduction of an explicit correlation factor in the Jastrow form (exponential) improves the variational energy, but this nodeless function does not improve the nodes of the system. Ideally, the Slater determinant needs be re-optimized in the presence of the correlation factor.

We have developed an algorithm to optimize trial function parameters (linear coefficients, non-linear exponential factors, and parameters of the correlation function) based on a random walk procedure. In order to obtain accurate energies for excited states, we introduce a projection operator method based on group theory to constrain the optimization process. It effectively distinguishes all the states of a given symmetry. We also apply the Young tableaux of permutation group theory to facilitate the treatment of fermion properties and multiplets.

Using an optimized trial function, we are studying pyramidal H_4 at the maximum ionicity excited state¹ (MIES) and other geometries relevant to understanding decomposition pathways in this system. The calculated potential energies show 0.6-0.8 eV lowering compared to a previous study¹. In a separate multi-configuration *ab initio* study we have determined that there is a pathway without a barrier for $H_2(B)$ approach to ground state $H_2(X)$. Work is in progress to fully characterize the first-excited state of the H_4 system and its coupling to the ground state, and will be discussed.

* This work was supported by the U.S. Air Force Rocket Propulsion Laboratory (AFRPL) through agreement with the Department of Energy under Contract No. DE-AC03-76SF00098.

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¹ C. A. Nicolaides, G. Theodorakopoulos, and I. D. Petsalakis, J. Chem. Phys. **80** (4), 1705 (1984).

QMC AND MCSCF STUDY OF TETRAHYDROGEN

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I. MCSCF Pilot Study of Trigonal Pyramidal Ground- and Excited-State H_4 .

We have demonstrated that MCSCF (multiconfiguration self-consistent field) wave functions as trial functions for FNQMC (fixed-node quantum Monte Carlo) calculations can recover ~100% of the correlation energy of ground states and ~95% of the correlation energy of excited states.¹ Using an extended (triple zeta-plus-polarization (TZP)) basis set, MCSCF calculations were carried out for the H_4 MIES (maximum ionicity excited state), see Fig. 1. They confirmed the characteristics depicted in Fig. 2 for the C_{3v} pyramidal structure including the minimum energy geometry, the doubly degenerate E ground state as H separates from H_3 for $R > 3.8$ a.u., and the nondegenerate A ground state for $R < 3.8$ a.u., consistent with an E- to A-state crossing at $R = 3.8$ a.u. For C_s symmetry the avoided crossing was obtained. Figure 3 displays the results of the MCSCF pilot computations. These curves lie above those of Nicolaides, Theodorakopoulos, and Petsalakis (NTP)² and reflect the better capability of the ab initio MRD-CI wave functions compared to the compact MCSCF trial functions needed here as FNQMC trial functions. The key comparison, however, will be with the FNQMC results obtained with the MCSCF functions. We discuss this point in Sec. III.

II. MCSCF Pilot Study of the $H_2(X) + H_2(B) \rightarrow H_4$ MIES Pathway.

Calculations were carried out for $H_2(B)$ approach to $H_2(X)$ in which these molecules are contained initially in perpendicular planes that bisect

each other. Figure 4 displays this arrangement and summarizes, in the accompanying table a sequence of geometry changes, labeled I-VII, that carry the system from the asymptotic region to the neighborhood of the H_4 MIES configuration. The table also contains the energy lowering associated with the steps that are plotted in Fig. 5. It is noteworthy that no energy barrier is encountered along this path. Further, Fig. 6 shows that when $H(B)$ is displaced from bisecting $H_2(X)$ in step II, charge transfer immediately occurs. (Similar behavior has been found for the related $H_2(B) + He$ system in an independent study by WAL.)

III. FNQMC Study of the Ground-State Pyramidal Structure for C_{3v} Symmetry

FNQMC calculations using the MCSCF trial functions discussed in Sec. I yield ~ 0.6 – 1.0 eV energy lowering compared to the results of NTP and are presented in Fig. 7. Such a large change was not anticipated and so it was important to test the validity of this finding. To this end a configuration interaction calculation including all single and double excitations (SDCI) using the MCSCF pilot study basis set was carried out at $R = 3.4$ a.u. The energy was 0.32 eV lower than NTP's value and is consistent with the improvement expected based on studies of other systems. The FNQMC results of Fig. 7 obtained using a new trial function optimization algorithm, see Sec. IV, are generally an improvement over those of Fig. 7 obtained using MCSCF trial functions.

IV. FNQMC Study of the Excited State

These calculations provide the severest test of the FNQMC approach because

of the lack of knowledge of the accuracy of the excited state trial function needed to provide a nodal description that assures orthogonality to the ground state of the same (A') symmetry (C_s). MCSCF calculations close to the avoided crossing suffered from root flipping. Despite the use of familiar MCSCF strategies to address the problem, it could not be resolved.

The MCSCF convergence problem had been encountered earlier for $\text{He} + \text{H}_2(\text{B})$ but resolved by the use of an ab initio CI method. Interest here in using the FNQMC method led us to develop a method for trial function construction³ that avoids the MCSCF procedure. The approach amounts to the introduction of parameter optimization in the random walk process. Using group theory a projection operator is constructed and used to constrain the wave function to have the symmetry properties of the state of interest. This method has been employed in the present effort to generate the A-state FNQMC results, denoted A(FNQMC), of Fig. 7. Calculations using this method are in progress to complete the E-state curve, labeled E(FNQMC), in Fig. 7 for $3.8 < R < 6.0$ a.u.

V. SA-MCSCF Study of Distorted Geometries

Calculations have been carried out using the state averaged (SA)-MCSCF method to develop trial functions for a QMC study of the topography of the ground- and excited-state potential energy surface (pes) in the region of the symmetric geometry of the MIES determined by NTP. Figure 8 presents the coordinate system, Fig. 9 provides perspective views, and Fig. 10 ($R = 4.0$ a.u.) and Fig. 11 ($R = 3.8$ a.u.) show contour maps of the pes in the MIES region. Figures 10 and 11 show that the ground state has a saddle point at smaller R than the minimum of the excited state and that both features

correspond to an isosceles triangle base for the MIES system. Further geometry optimization is explored in Fig. 12 which plots potential energy as a function of d , the displacement of H_a towards the base of the H_3 isosceles arrangement. The minimum for the excited state is found for $d = 0.1$ a.u.

VI. Nonadiabatic Coupling

The stability of the MIES system is dependent on nonadiabatic coupling (NAC) to the ground state. Although the focus of this study is characterization of the region of pes of the MIES, the need to ascertain first the stability of the excited system is a high priority here because of the effort associated with the trial function optimization method and the expense of QMC calculations with small statistical variances. To calculate the NAC matrix elements we took advantage of the simplifications made possible by the use of normal mode distortions (Fig. 13) from the highly symmetric C_{3v} symmetry. Our calculations show that nuclear displacements associated with modes Q_1 and Q_2 lead to strong coupling between the A and E states. Relatively weaker coupling is found in Q_4 and Q_5 . The two totally symmetric modes (Q_3 and Q_6) give no contribution.

The size of the NAC matrix elements connecting the A' state to the E-state components (C_{3v} notation is used here to indicate parentage) are tabulated in Fig. 14 for the minimum energy geometry of the A state. These results establish that there is strong coupling between these states. Further computational study is needed to confirm these predictions and estimate reliably, the excited state lifetime.

References and Footnotes

[†]Also, Department of Chemistry, University of California, Berkeley 94720.

¹R. M. Grimes, B. L. Hammond, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. 85, 4749 (1986).

²C. A. Nicolaides, G. Theodorakopoulos, and I. D. Petsalakis, J. Chem. Phys. 80, 1705 (1984).

³S.-Y. Huang, Z. Sun, and W. A. Lester, Jr., "Algorithm for Optimizing Parameters in a Quantum Monte Carlo Trial Function," to be published.

Figure Captions

Figure 1. MIES coordinate system (assuming C_{3v} symmetry): R is the distance from H_a to plane of $H_bH_cH_d$ equilateral triangle of side r .

Figure 2. Ground- and excited-state H_4 potential energy curves for trigonal pyramidal geometry: upper panel (C_{3v} symmetry), lower panel (C_s symmetry).

Figure 3. Potential energy curves from MCSCF trial functions for trigonal pyramidal geometry and C_{3v} symmetry ($r = 1.70$ a.u.). State designations for C_s symmetry are indicated in parentheses. The lack of coincidence of the degenerate E curves reflects their calculation in lower symmetry and provides an indication of MCSCF convergence.

Figure 4. Geometries used to calculate an approach of $H_2(B)$ to $H_2(X)$.

Figure 5. Plot of total energies corresponding to the pathway presented in Figure 4.

Figure 6. Change of charge distribution between H_a and H_b as a function of d , the displacement of the midpoint of $H_2(B)$ above the plane of $H_2(X)$.

Figure 7. Potential energy of trigonal pyramidal H_4 versus R . The A (variational) results were determined using a new optimization method for QMC trial functions.

Figure 8. MIES coordinate system used for geometry variation. d is the magnitude of the displacement of H_a along the bisector of the H_cH_d side of length b .

Figure 9. Potential energy surfaces for the ground- and excited-state separately for easy visualization and in computed relative positioning. Note the minimum of the excited state and saddle point of the ground state.

Figure 10. Potential energy contour map for $R = 4.0$ a.u. as a function of a and b ; see Fig. 8.

Figure 11. Same as Fig. 10 for $R = 3.8$ a.u.

Figure 12. Potential energy curves for selected R (in a.u.) vs d ; see Fig. 8.

Figure 13. Normal mode displacements of H_4 in C_{3v} symmetry.

Figure 14. CI contribution to coupling matrix elements for normal mode displacement, see Fig. 13.

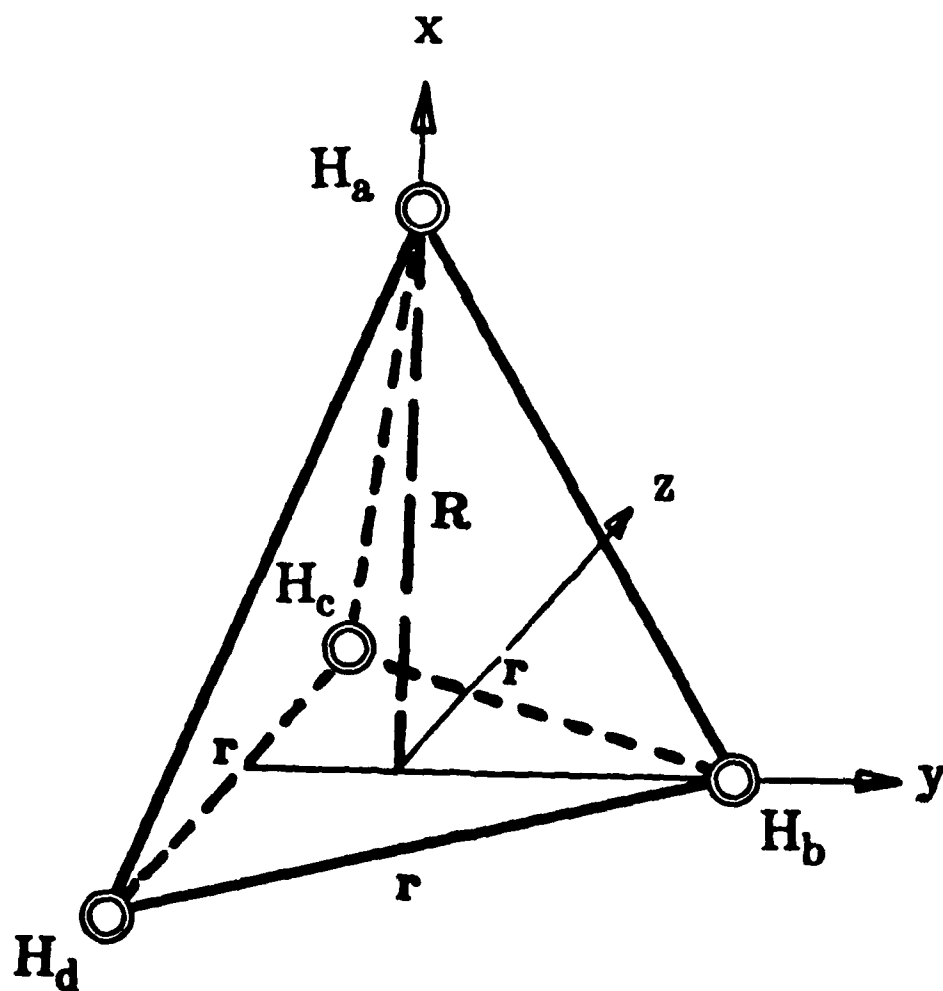


Fig. 1

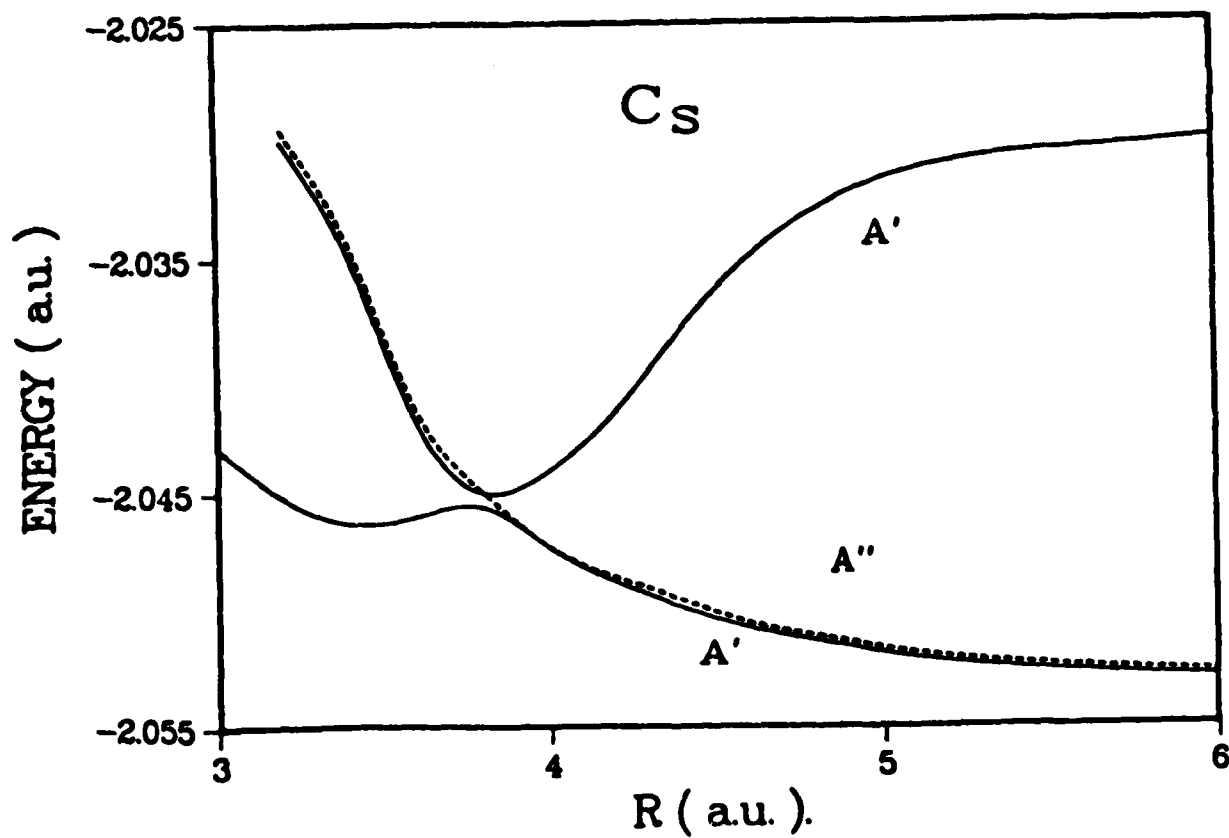
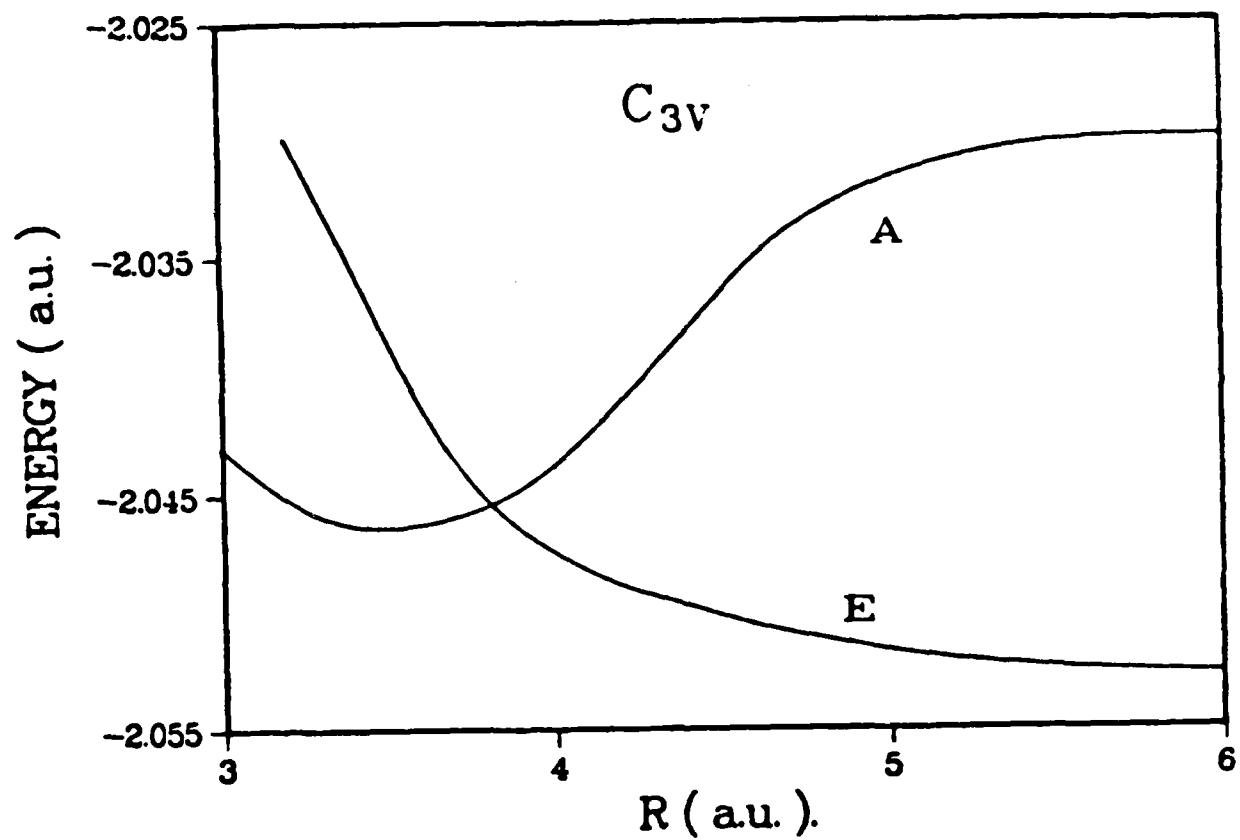


Fig. 2

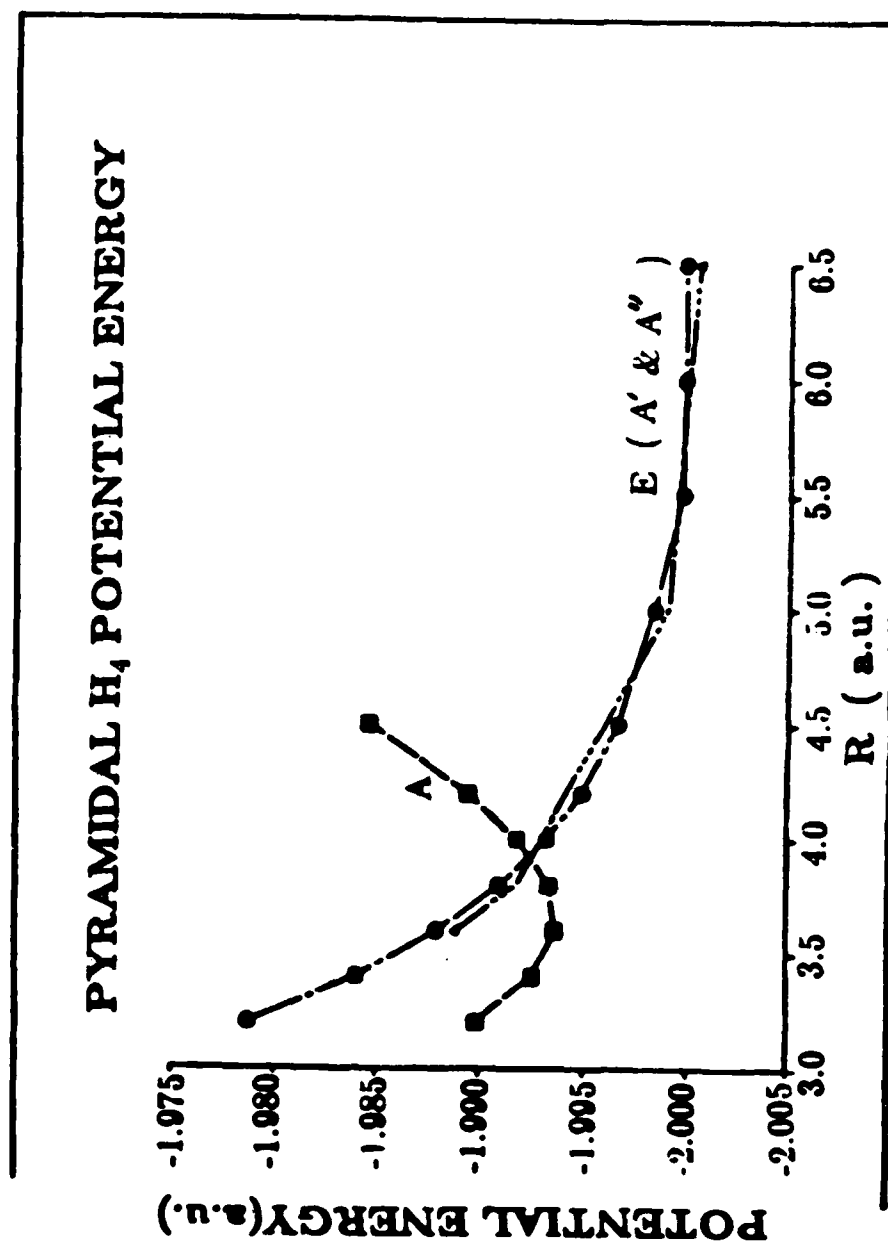


Fig. 3

Geometries and energies for the approach of $H_2(B)$ to $H_2(X)$

step	R'	L_1	L_2	$L_2(+)$	$L_2(-)$	D	energy lowering
I	5-2.2	1.40	2.43	1.215	1.215	0.0	-0.91
II	2.2	1.40	2.43	1.215-1.93	1.215-0.5	0.715	-0.20
III	2.2	1.60	2.63	1.93-2.13	0.5	0.865	-0.20
IV	2.2-1.75	1.60	2.63	2.14	0.5	0.865	-0.20
V	1.75-1.55	1.60	2.73	2.23	0.5	0.915	-0.46
VI	1.55	1.60	3.13	2.23-2.63	0.5	1.115	-0.69
VII	1.50	1.70	3.23	2.63-2.73	0.5	1.165	-0.11

TOTAL ENERGY LOWERING FOR THE SEVEN STEPS IS 3.75 ev.

* Distances in a.u.; energies in ev.

R' - distance between the midpoint of $H_2(X)$ and the point where $H_2(B)$ meets the $H_2(X)$ plane.

L_1 - length of $H_2(X)$.

L_2 - length of $H_2(B)$.

$L_2(+)$ - length of $H_2(B)$ above $H_2(X)$ plane.

$L_2(-)$ - length of $H_2(B)$ below $H_2(X)$ plane.

D - magnitude of shift of $H_2(B)$ midpoint (above (+)/below(-)) plane of $H_2(X)$.

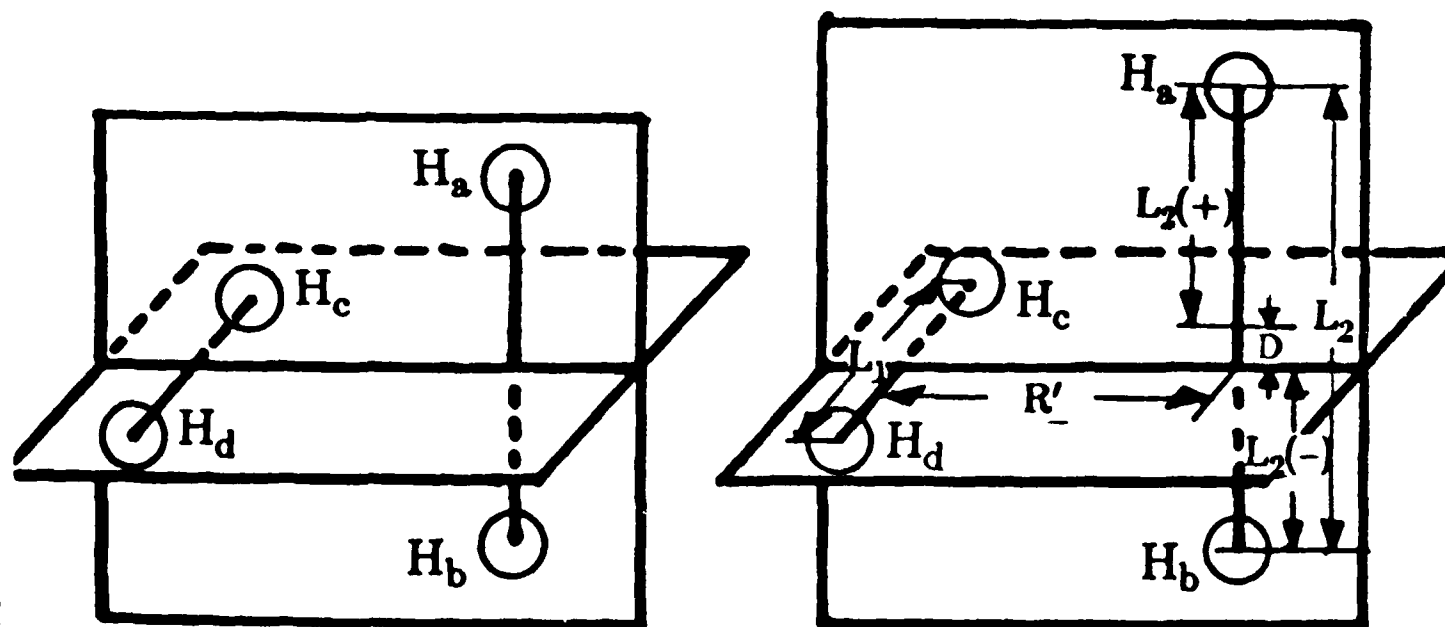


Fig. 4

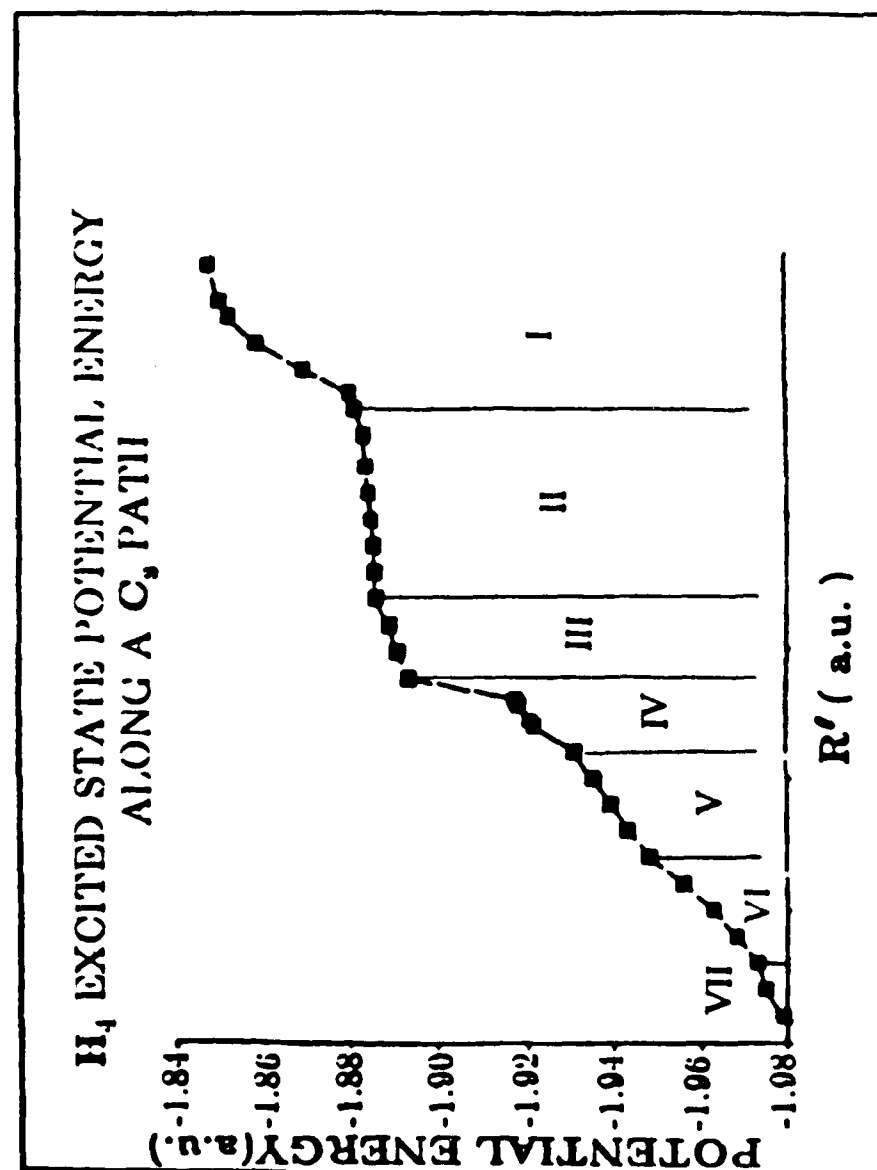


Fig. 5

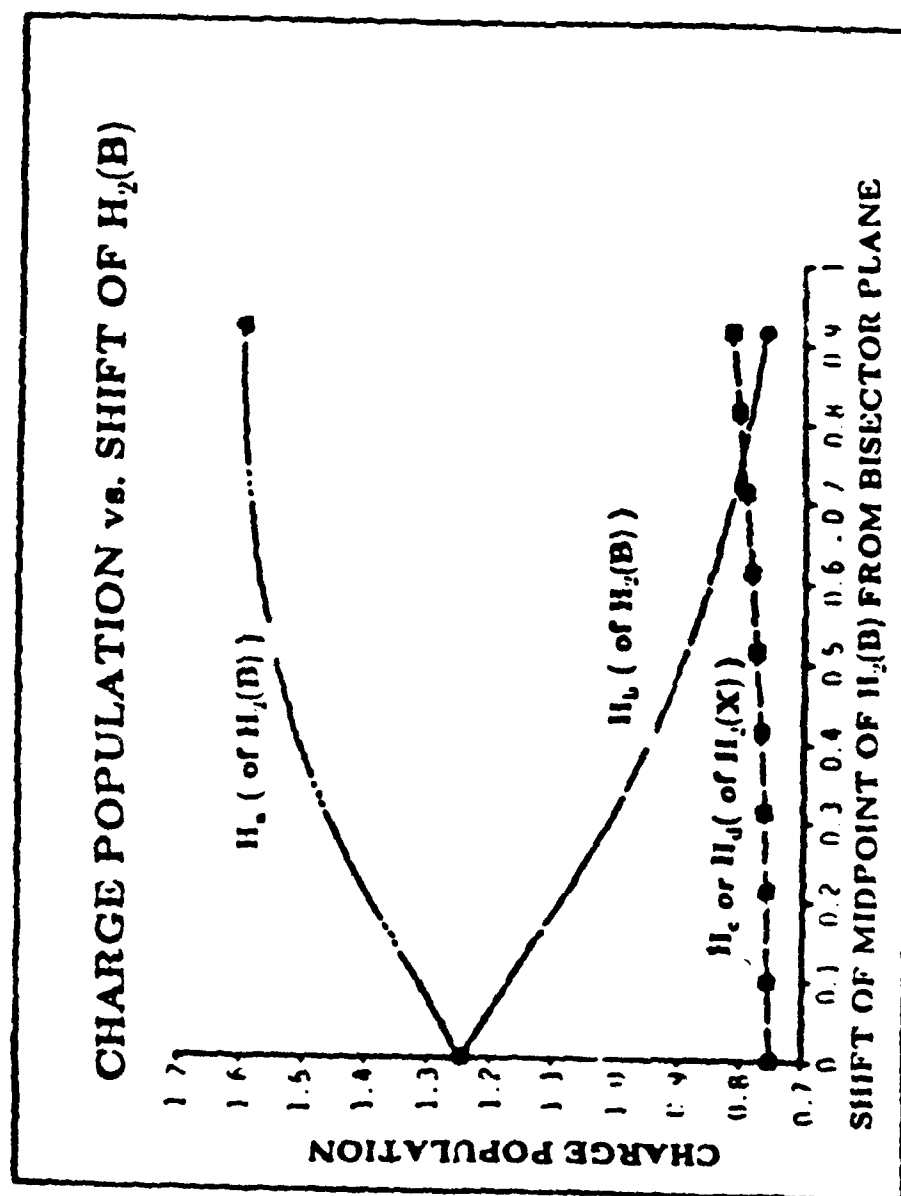


Fig. 6

POTENTIAL ENERGY OF PYRAMIDAL H_4

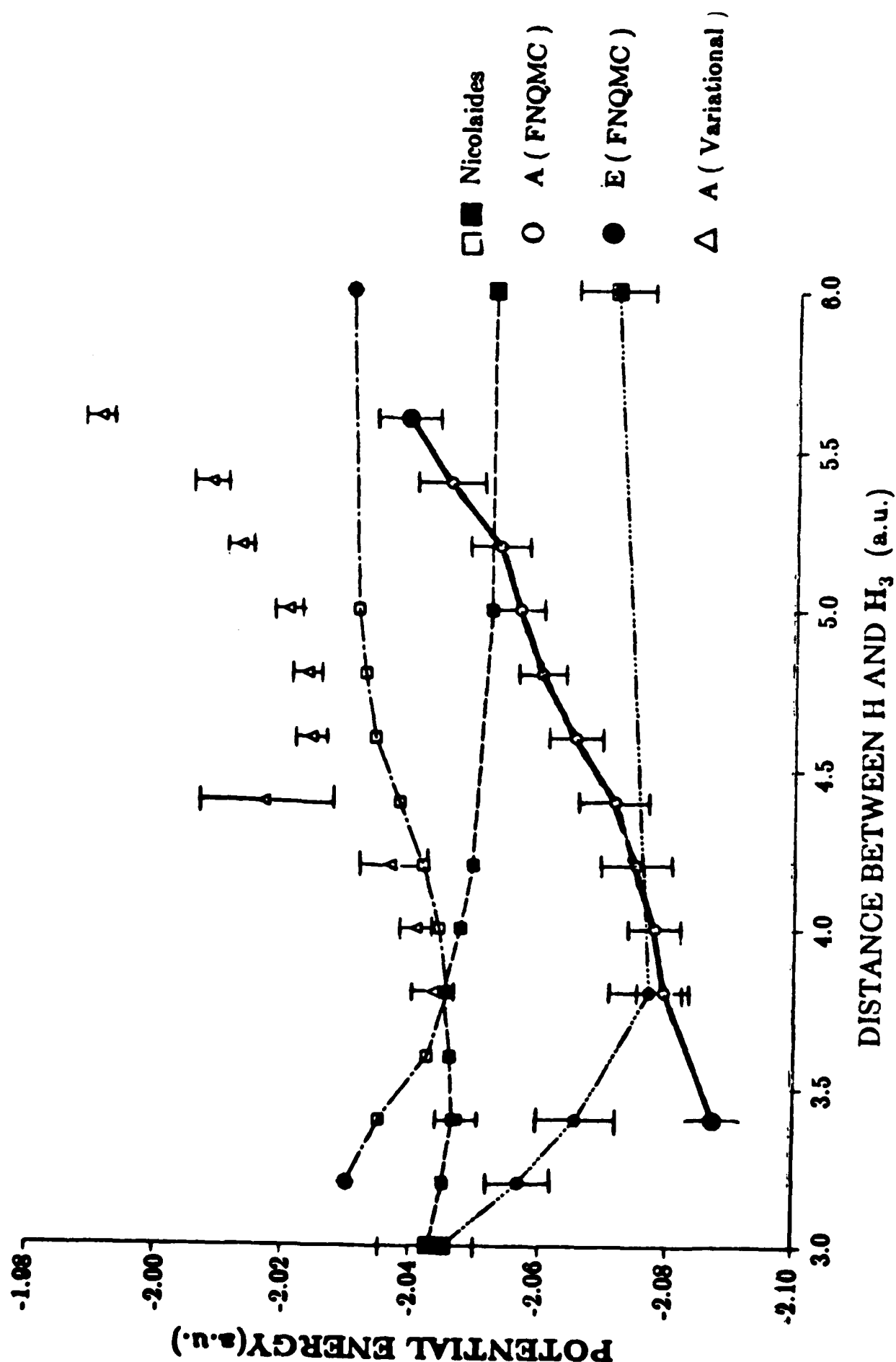


Fig. 7
139

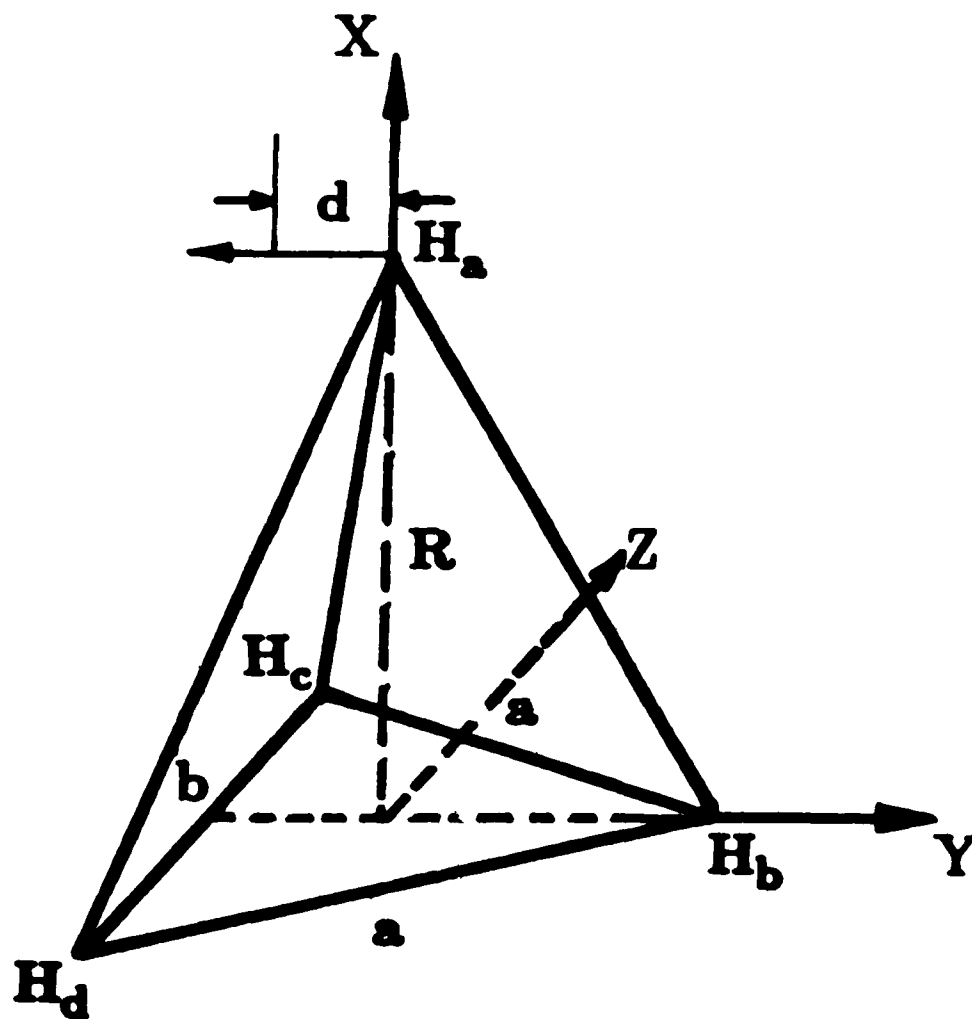
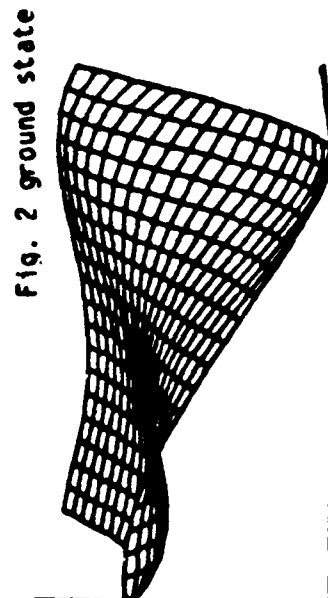
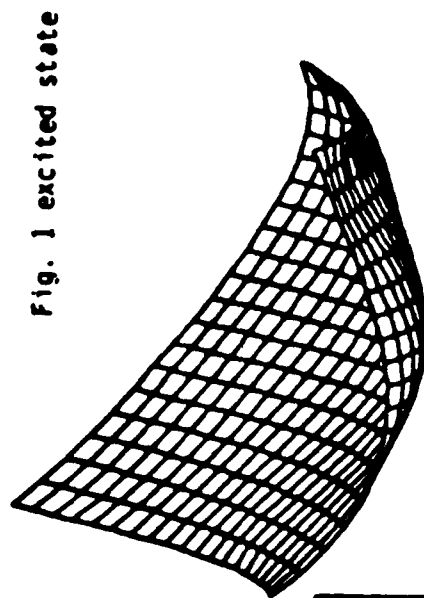
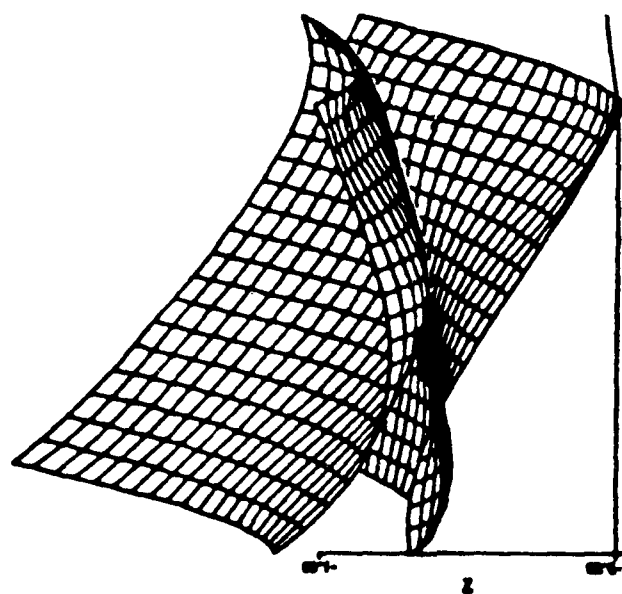


Fig. 8



Q (1.5-1.9 a.u.)
b (1.4-2.0 a.u.)
E (-2.03 -1.08 a.u.)



CONTOUR MAP ($R=4.0$ a.u.)

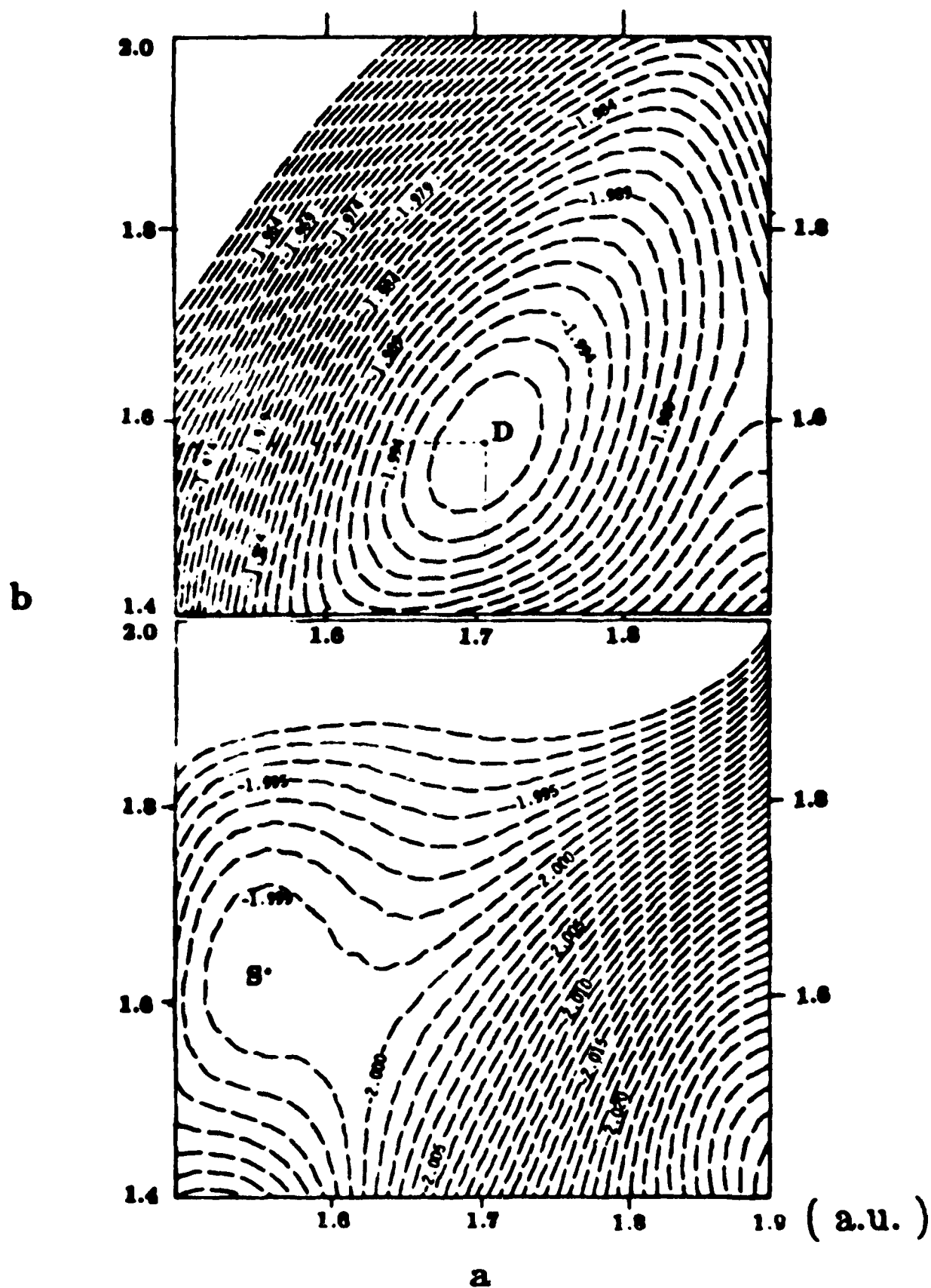


Fig. 10
142

CONTOUR MAP (R=3.8 a.u.)

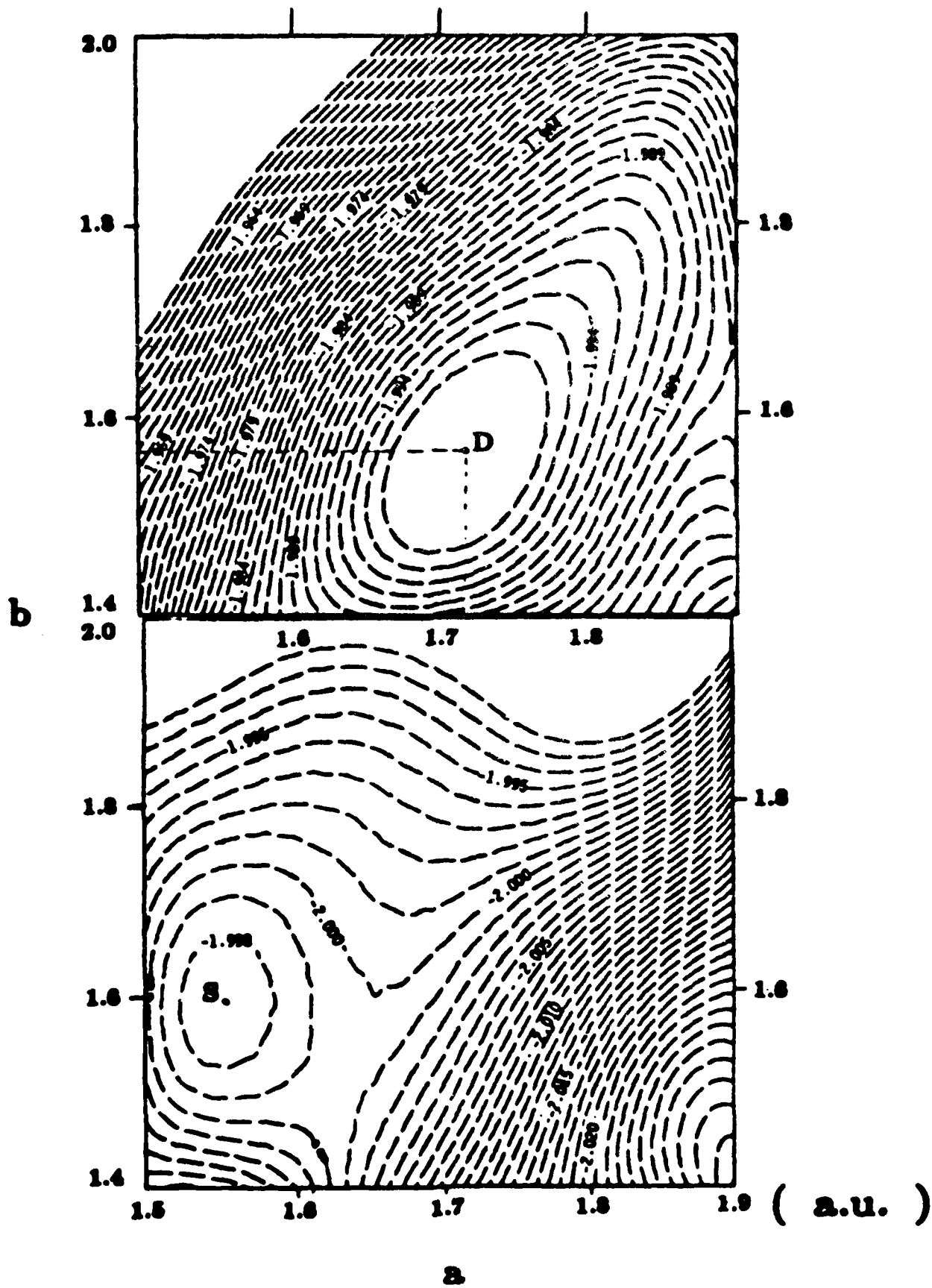


Fig. 11

POTENTIAL ENERGY V_s d

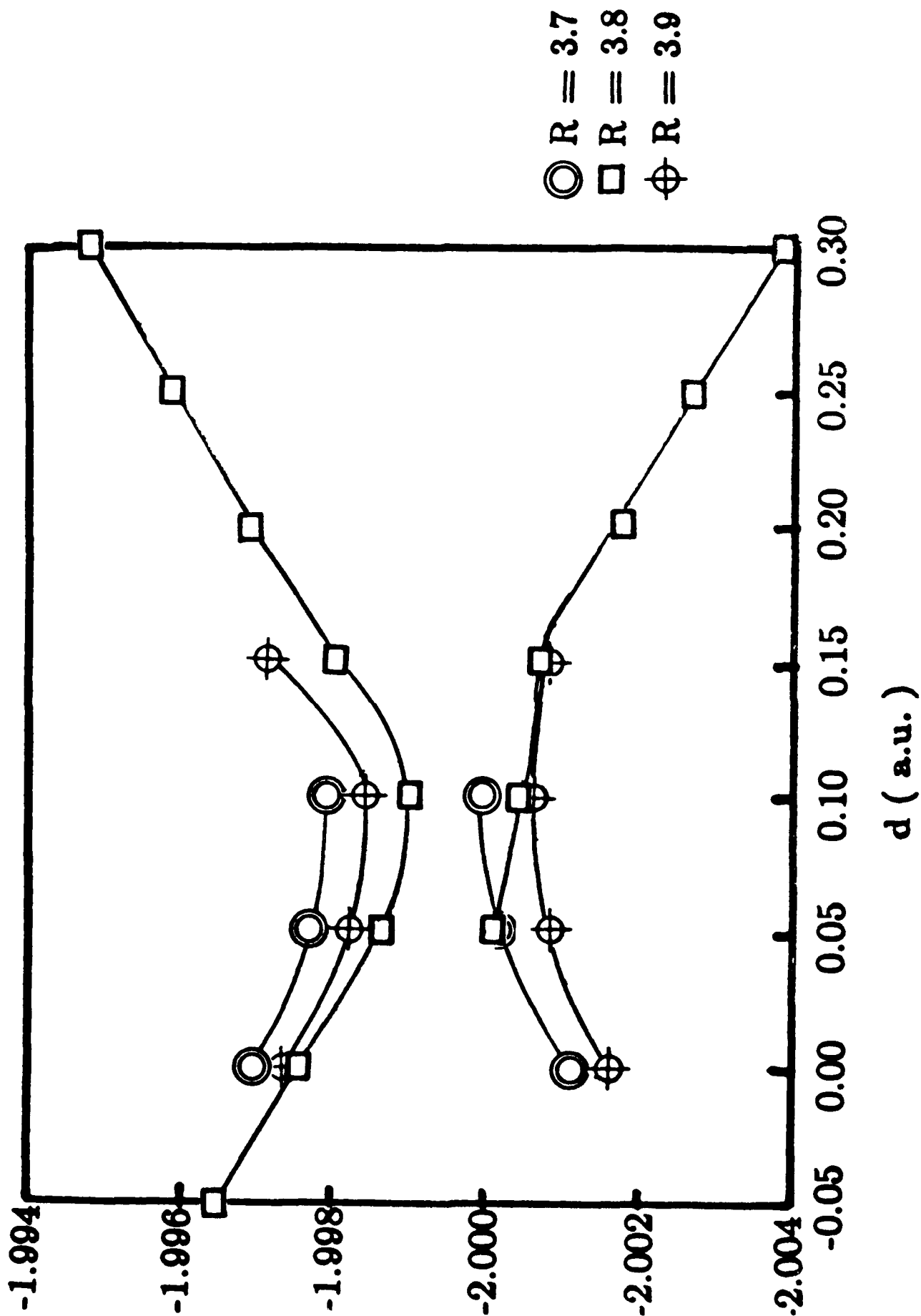


Fig. 12
144

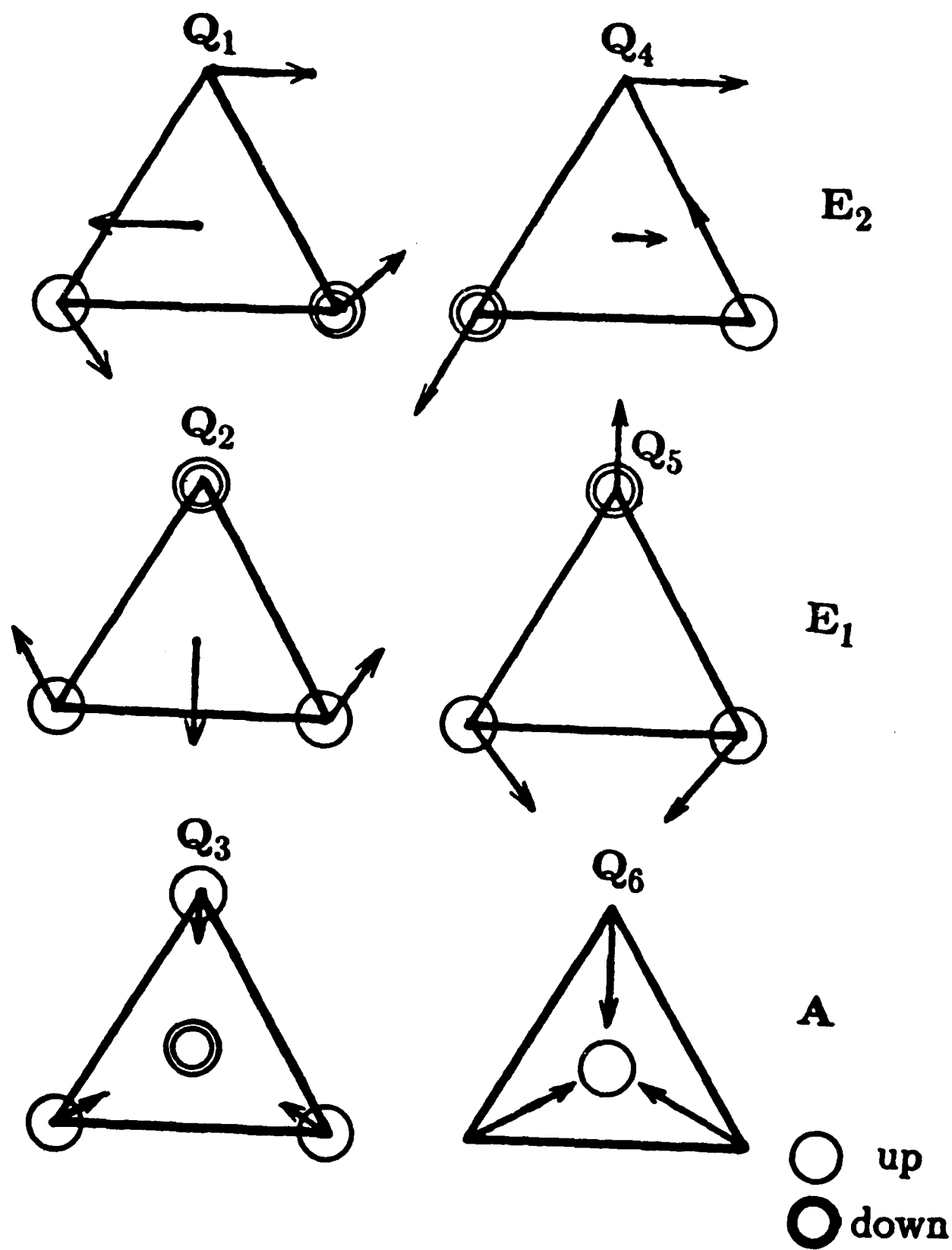


Fig. 13

Coupling matrix elements D^{CI} by a finite difference method (extrapolated from $\delta Q=0.002, 0.001, \text{ and } 0.0005$).

	$\langle E_2 A' \rangle$	$\langle E_1 A' \rangle$
Q_1	-2.0112(64)	0.0015(0)
Q_2	0.0017(0)	2.0127(98)
Q_3	0.0000	0.0000
Q_4	-0.3904(389)	-0.0010(3)
Q_5	-0.0039(13)	-0.3113(196)
Q_6	0.0000	0.0000

1. E_1 and E_2 are doubly degenerate states where E_1 is symmetric and E_2 is antisymmetric.

Fig. 14

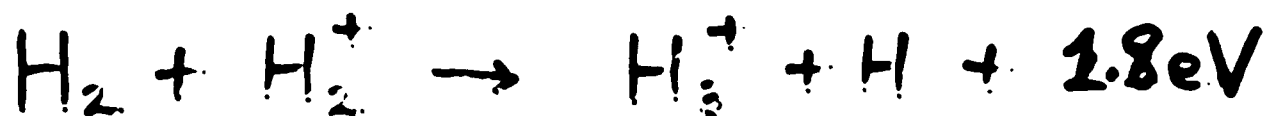
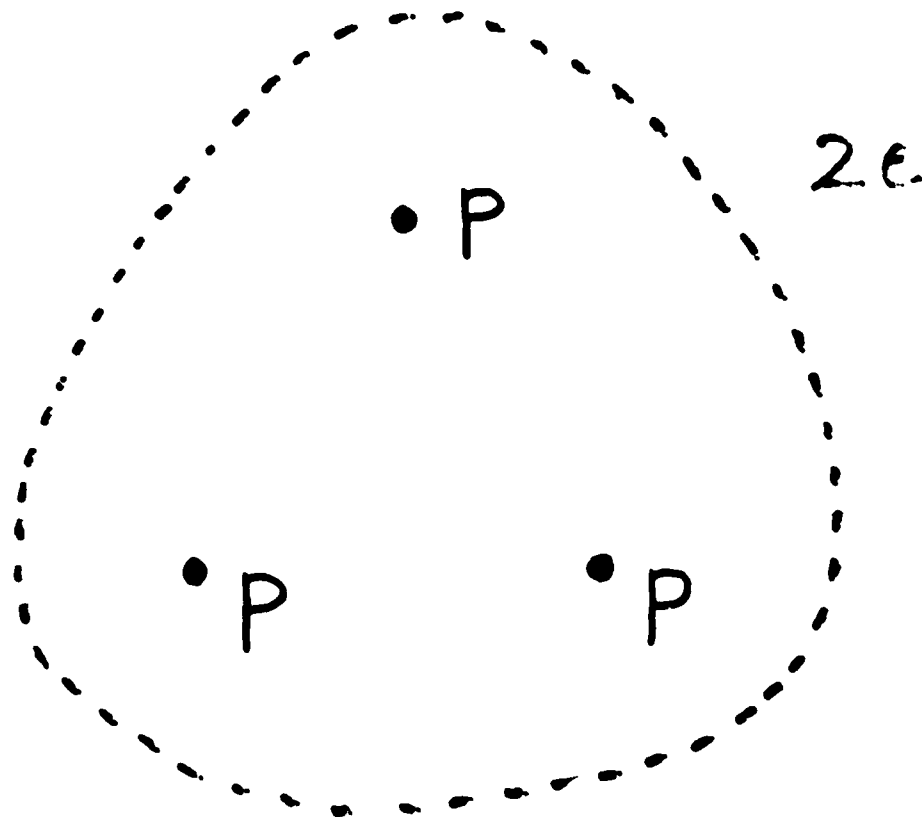
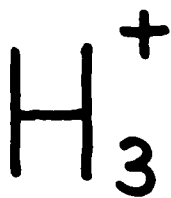
Abstract for HEDM Conference
Spectroscopy of Polyatomic Hydrogen Ions

Takeshi Oka

Infrared laser spectroscopy of the ν_2 -fundamental band of H_3^+ and the extension of work towards higher energy state and isotopic species will be reported. The chemical and physical dynamics of this ion in gaseous discharge will be discussed. Our plan to observe spectra of H_3^+ and its cluster ions in condensed phase plasma will be discussed.

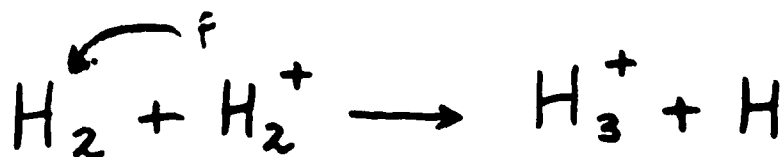
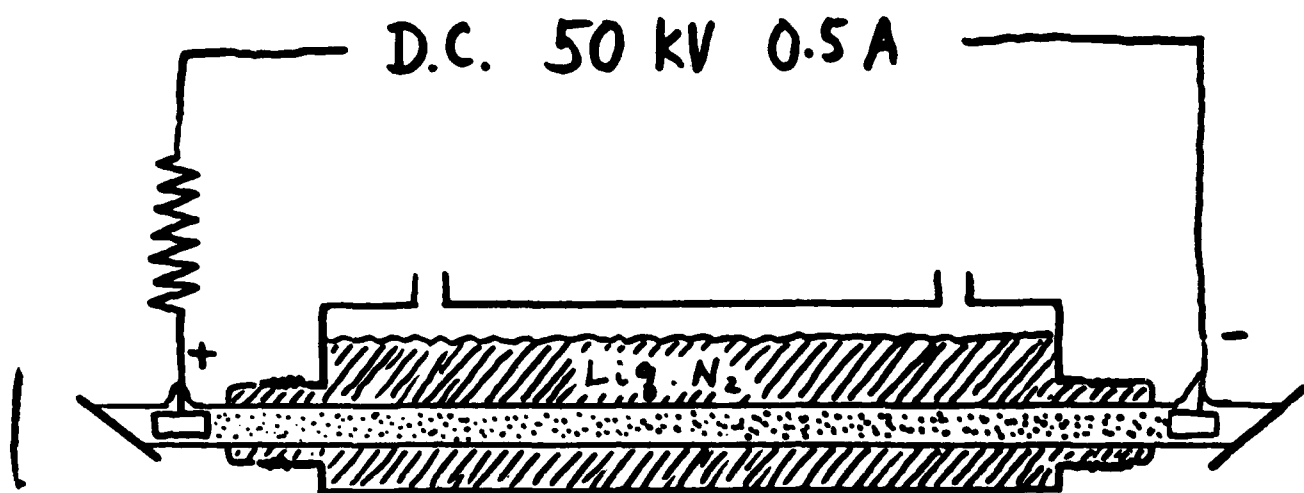
References

- T. Oka, Phys. Rev. Lett. 45, 531 (1980).
T. Oka, Phil. Trans. Roy. Soc. Lond. A303, 543 (1981).
T. Oka, "Laser Spectroscopy V", pp. 320, Springer-Verlag (1981).
T. Oka, "Molecular Ions: Spectroscopy, Structure and Chemistry", pp. 73, North-Holland (1983).
J.K.G. Watson, S.C. Foster, A.R.W. McKellar, P. Bernath, T. Amano, F.S. Pan, M.W. Crofton, R.S. Altman and T. Oka, Can. J. Phys. 62, 1875 (1984).
F.C. Foster, A.R.W. McKellar, I.R. Peterkin, J.K.G. Watson, F.S. Pan, M.W. Crofton, R.S. Altman and T. Oka, J. Chem. Phys. 84, 91 (1986).
F.S. Pan and T. Oka, Ap. J. 305, 518 (1986).
F.S. Pan and T. Oka, Phys. Rev., in press.



$$\sigma \sim 100 \text{ \AA}^2$$

Hydrogen Discharge

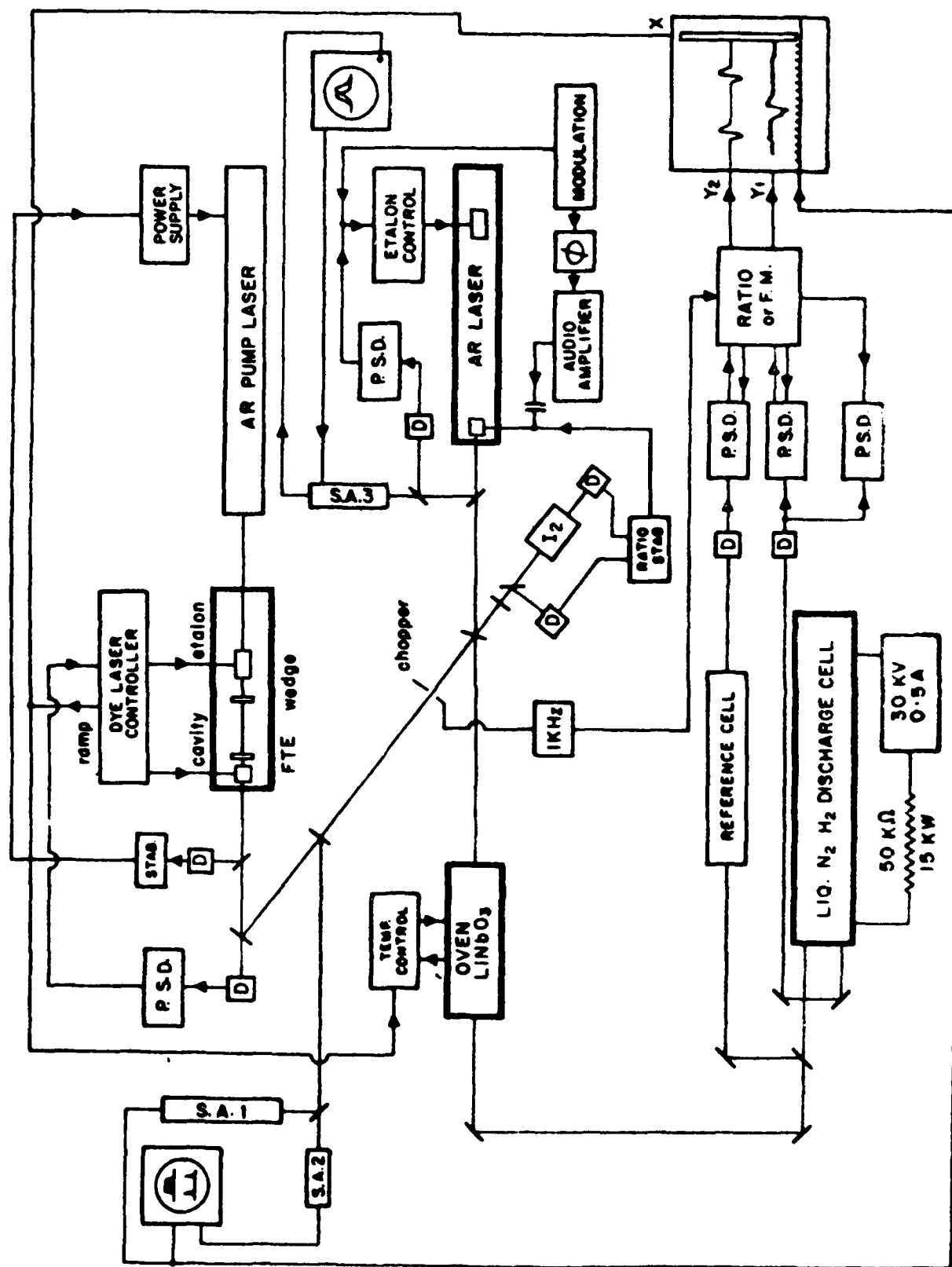


Energy $\lesssim 0.1 \text{ eV}$

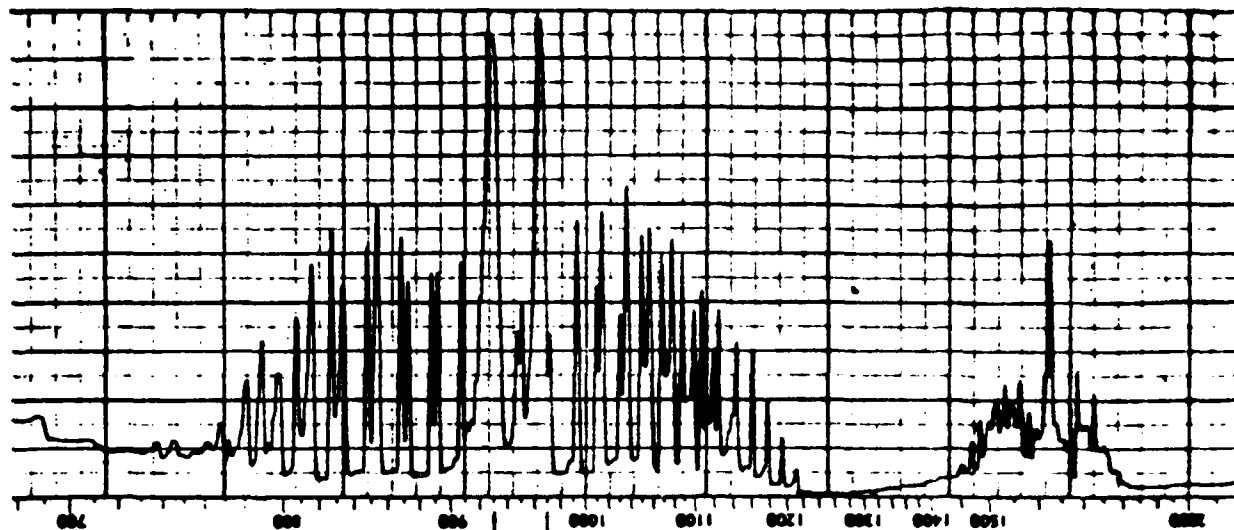
Discharge tube 2m, 2cm ϕ $\frac{[H_3^+]}{[H_2]} \sim 10^{-6}$
 $n(H_3^+) \sim 3 \times 10^{10} / \text{cm}^3$

Column Density $\sim 10^{14} / \text{cm}^2$

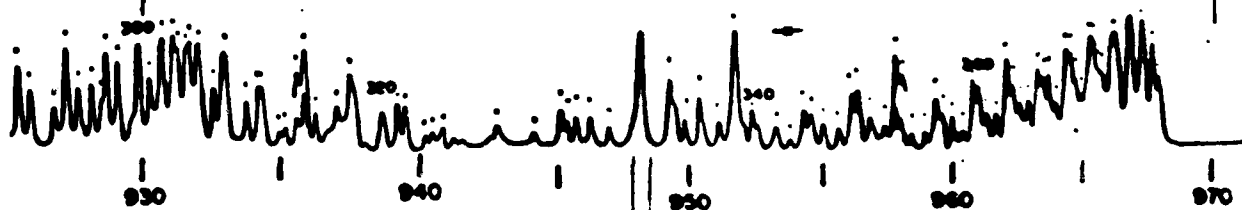
Temperature $\sim 200 \text{ K}$



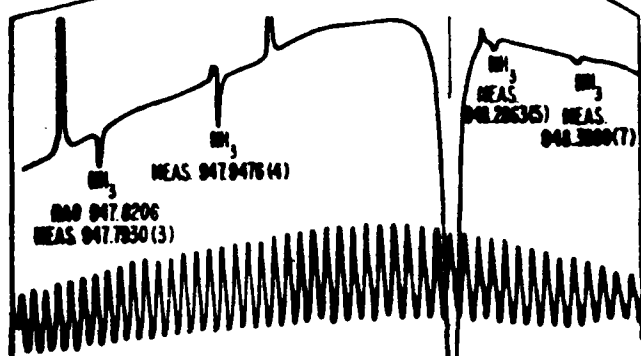
NH_3



X 20

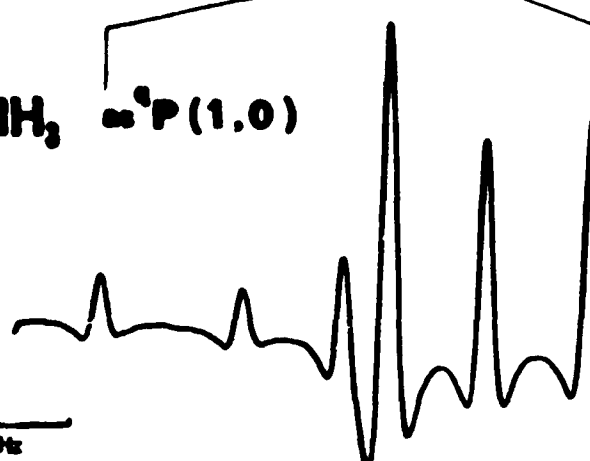


X 30



X 600

NH_3 $\pi^0\text{P}(1.0)$



X 30

1 MHz

Doppler-Ltd
Diode Laser

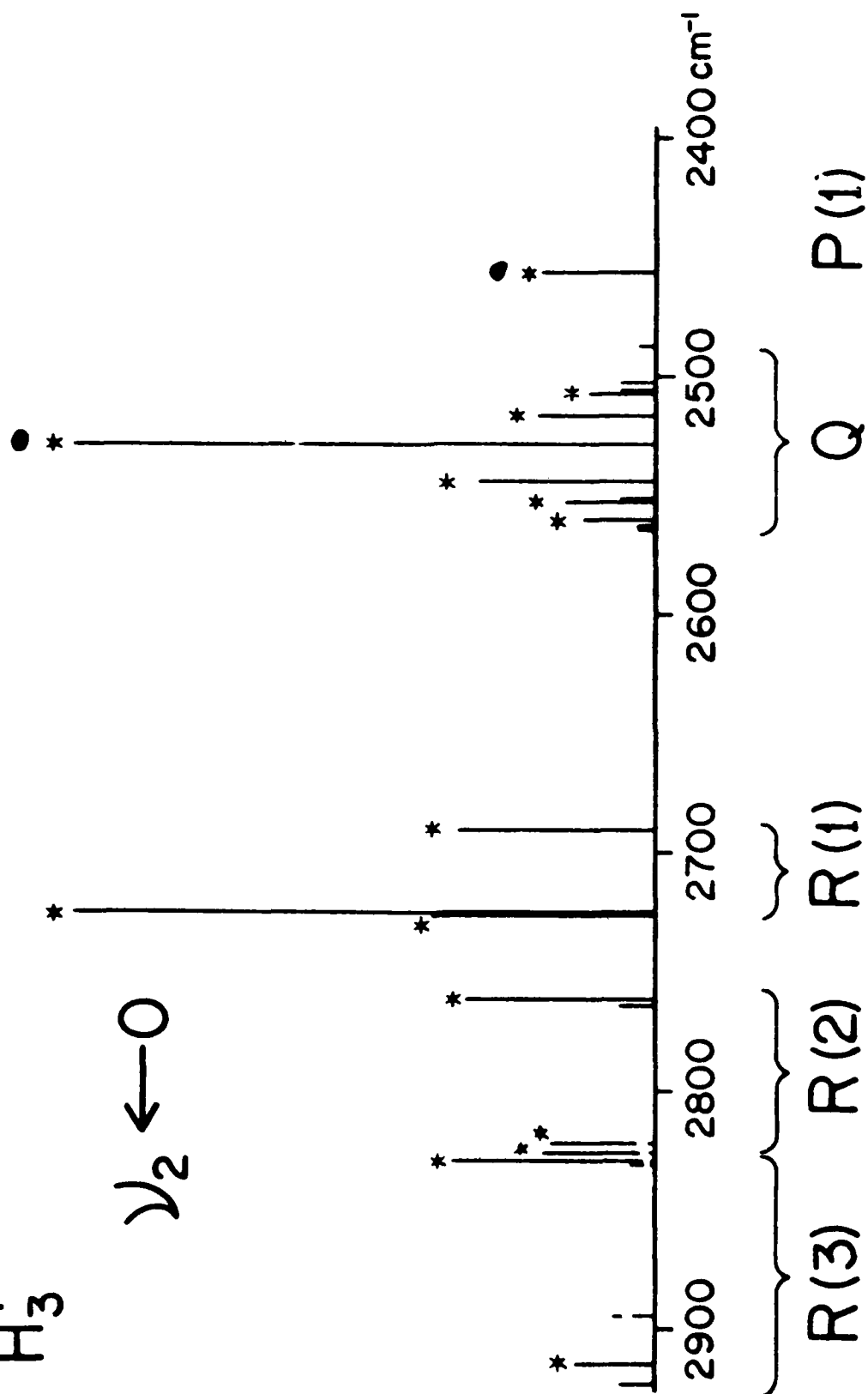
$$\frac{\Delta\nu}{\nu} \sim \frac{v}{c} \sim 10^{-6}$$

Sub-Doppler

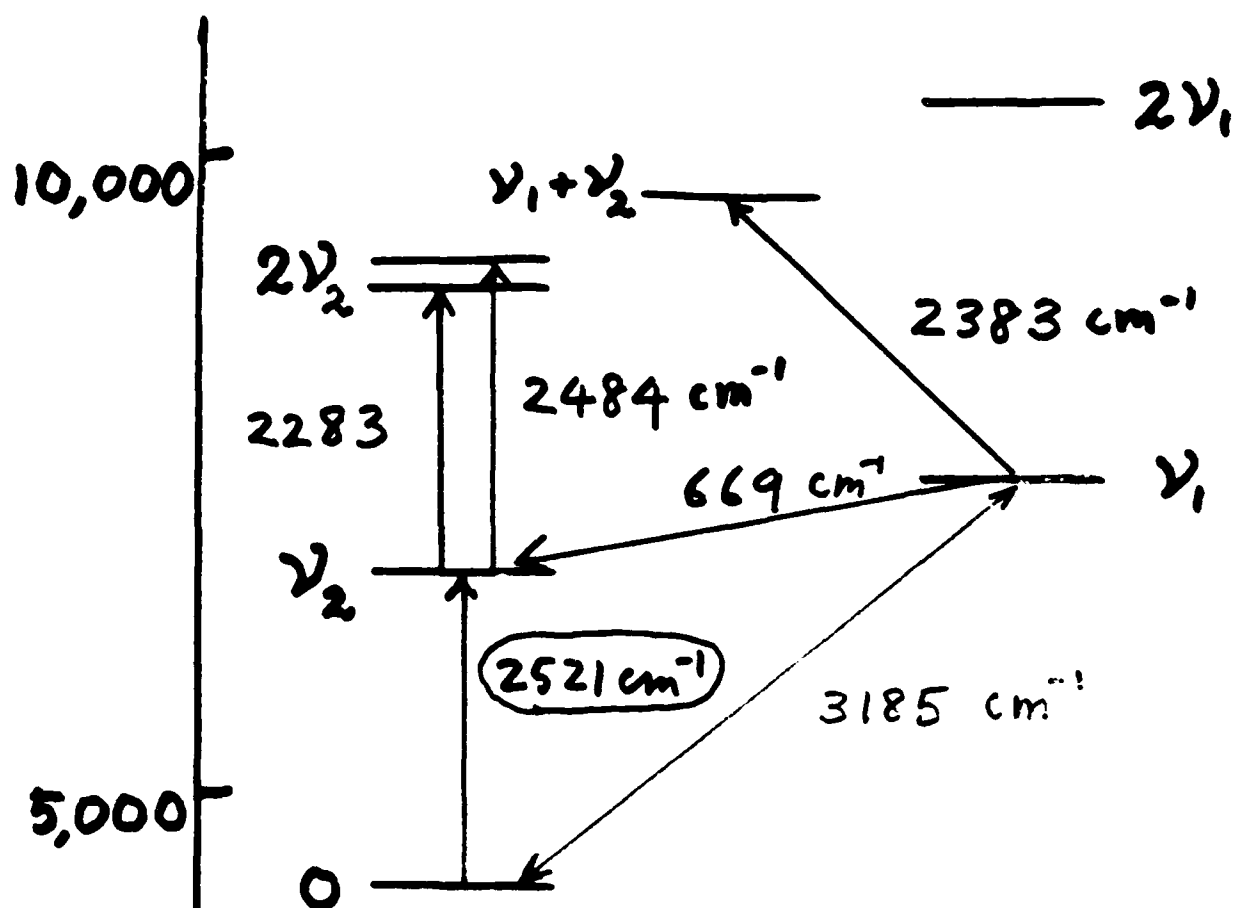
Chen, Frye,
OKA, J. Opt.
Soc. Am. (1986)

H_3^+

$\nu_2 \leftarrow 0$



H_3^+ vibrational states

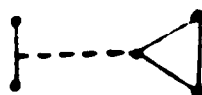


Carny^e + Porter (1976)

H_3^+ a)



$C_{2v}(I)$



$C_{2v}(II)$



D_{2d}



D_{2h}

$H_7^+(C_{2v})$



$H_9^+(D_{3h})$

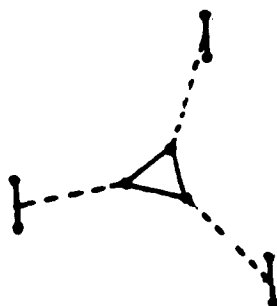
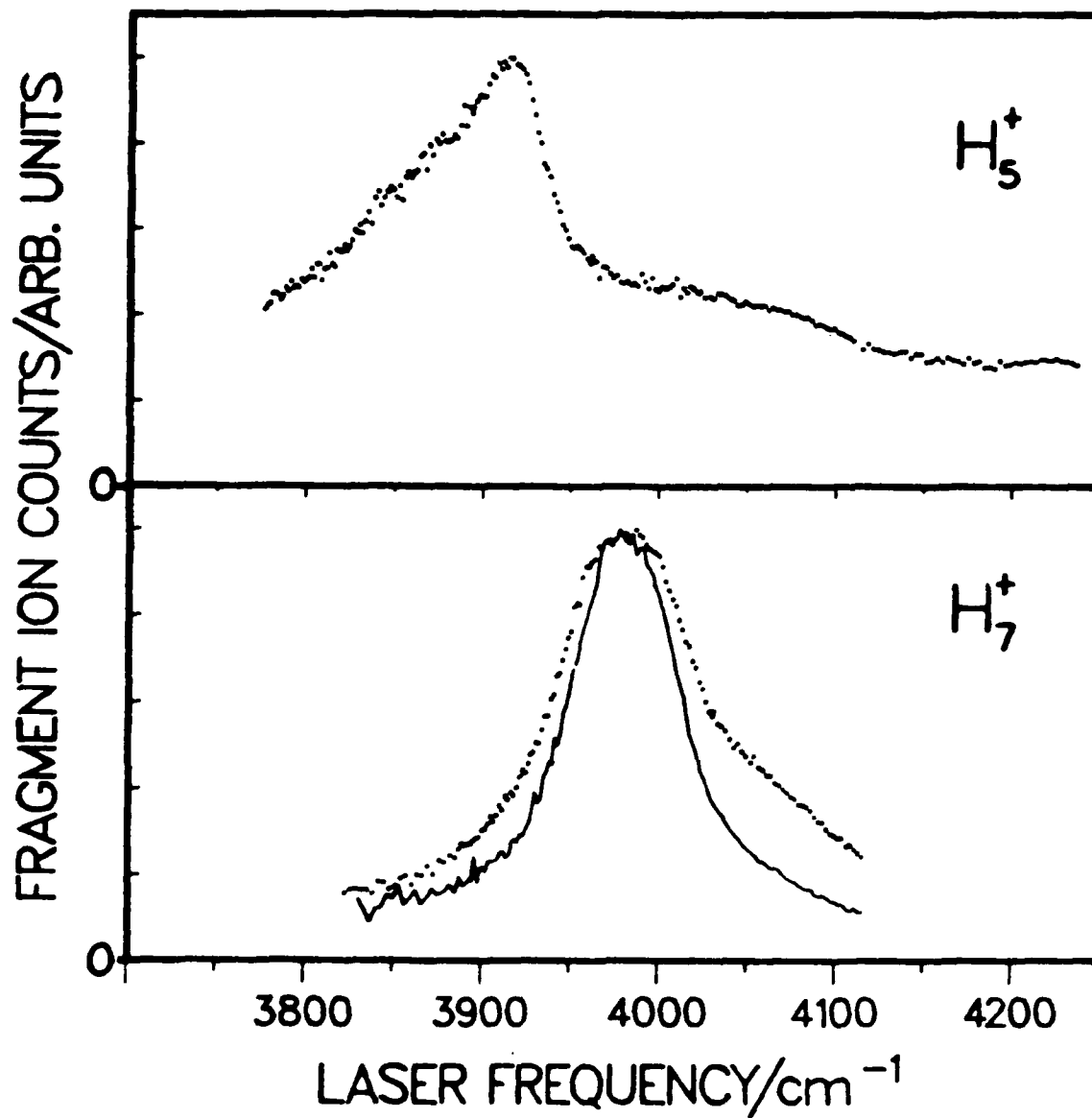


Fig. 5. Predicted optimum geometries of some cationic hydrogen clusters

a) Ahlrich predicts the relative stability $D_{2d} > D_{2h} > C_{2v}(I) > C_{2v}(II)$ whereas Yamaguchi *et al.* predict $C_{2v}(I) \sim C_{2v}(II) > D_{2d} > D_{2h}$

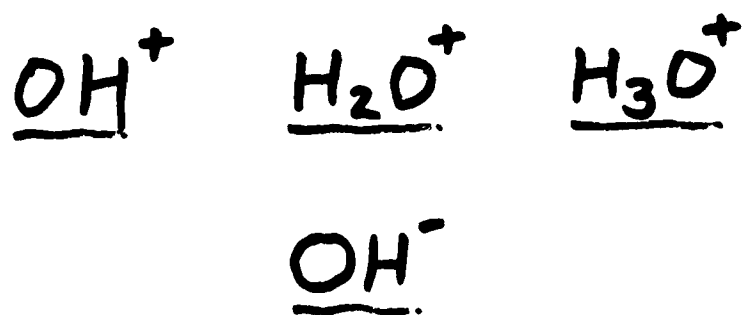
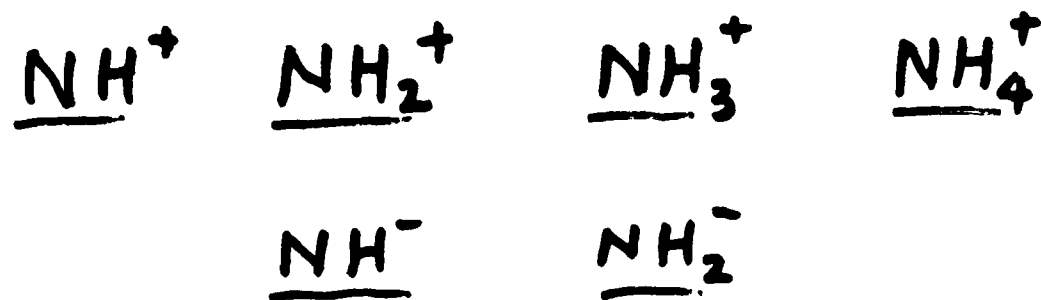
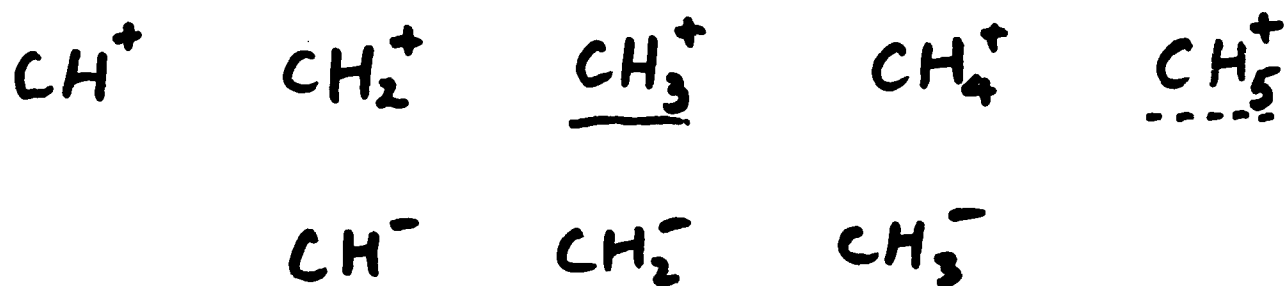
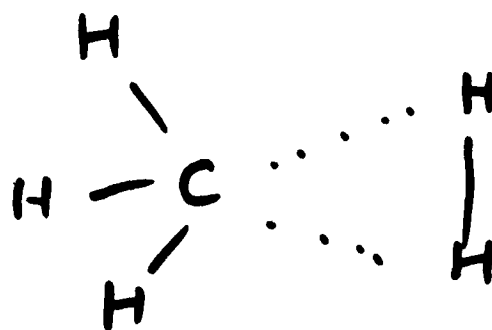
Ahlrich 1975
 Schaeter 1983, 1986



XBL 856-2839A

Fig. 1

Okumura, Yeh, and Lee (1985)



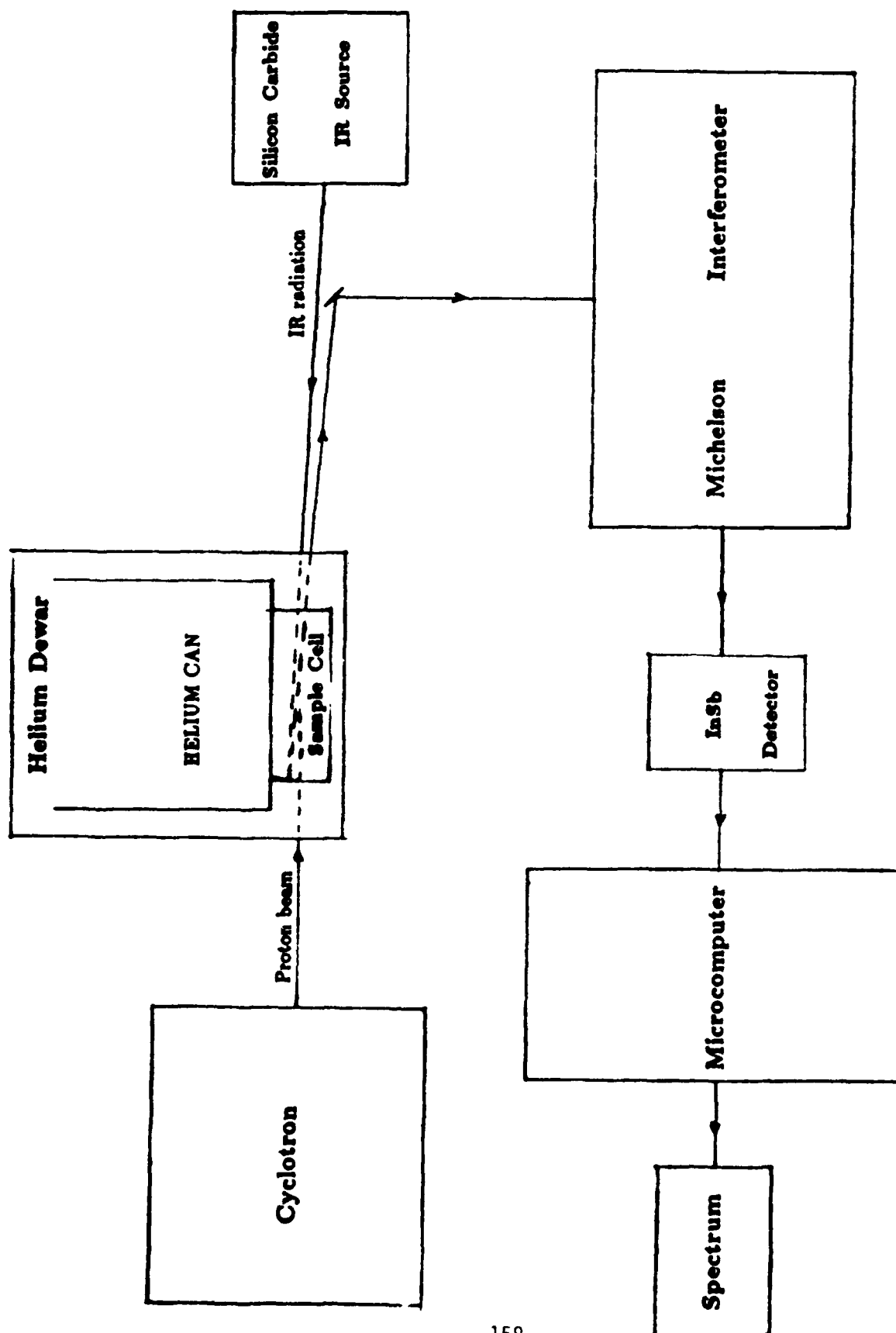


Fig. 1. Block diagram of the experimental set-up

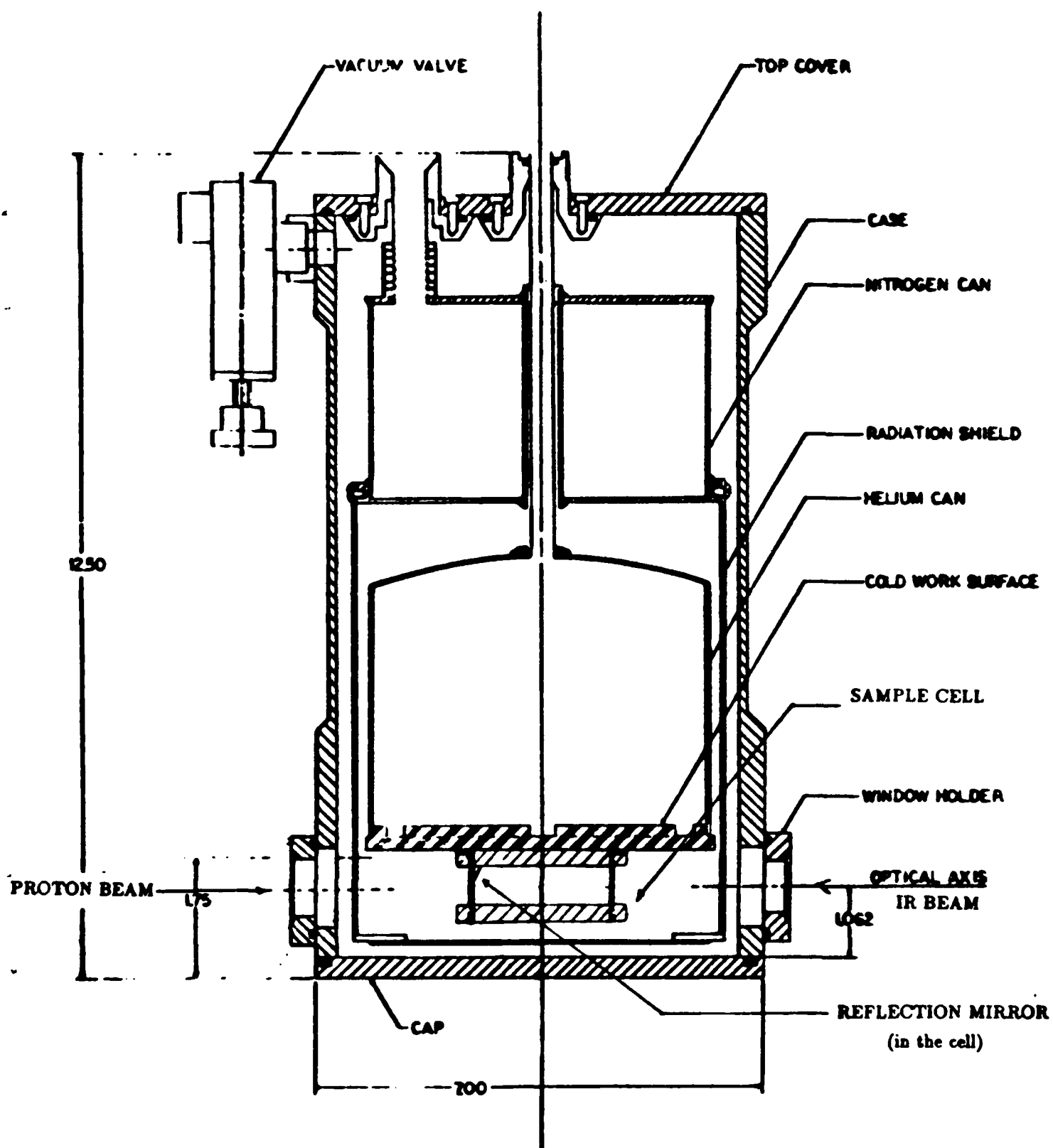


Fig. 2. Helium Dewar with the sample cell

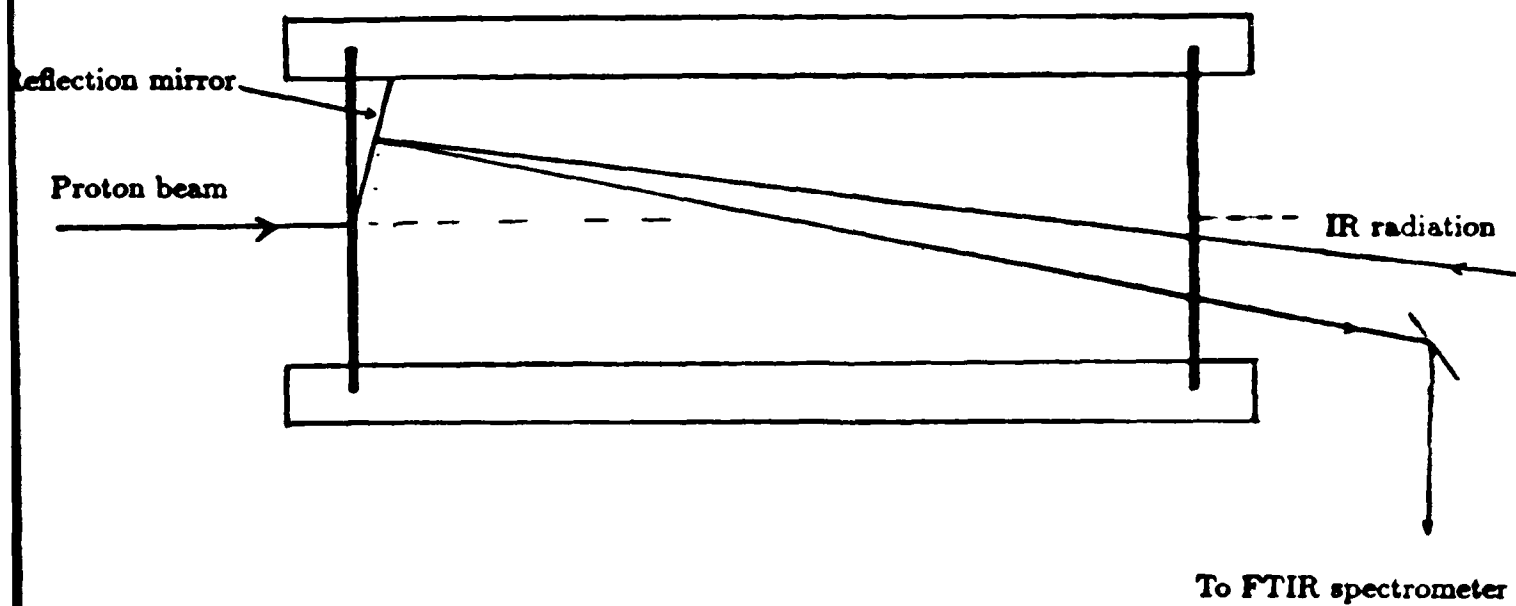
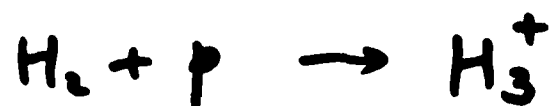
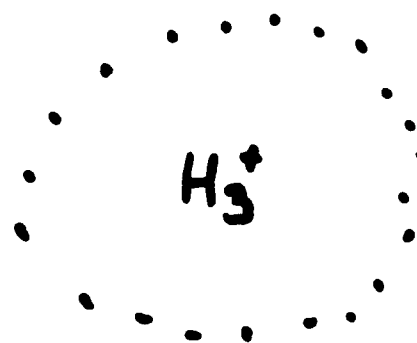
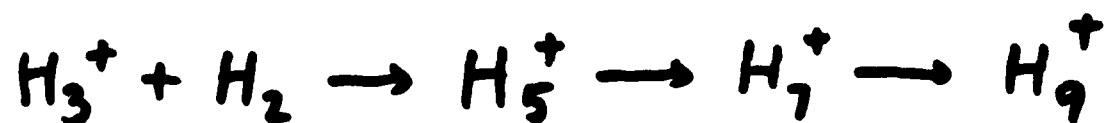
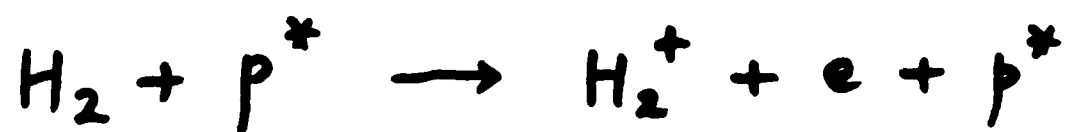


Fig. 4. Optical path in the sample cell



ADVANCED RESEARCH IN ENERGY STORAGE

**MAJ LARRY P. DAVIS
DR FRANCIS J. WODARCZYK**

**AFOSR/NC
MAY 1987**

OBJECTIVE

SEARCH FOR HIGH ENERGY DENSITY PROPELLANTS OR ENERGY CARRIERS

- LONG-LIVED ELECTRONIC EXCITED STATES
- CHEMICALLY METASTABLE SPECIES
- SPIN-POLARIZED SPECIES

HIGH ENERGY DENSITY MATERIALS

PROGRAM PLAN

HIGH ENERGY GROUND STATES

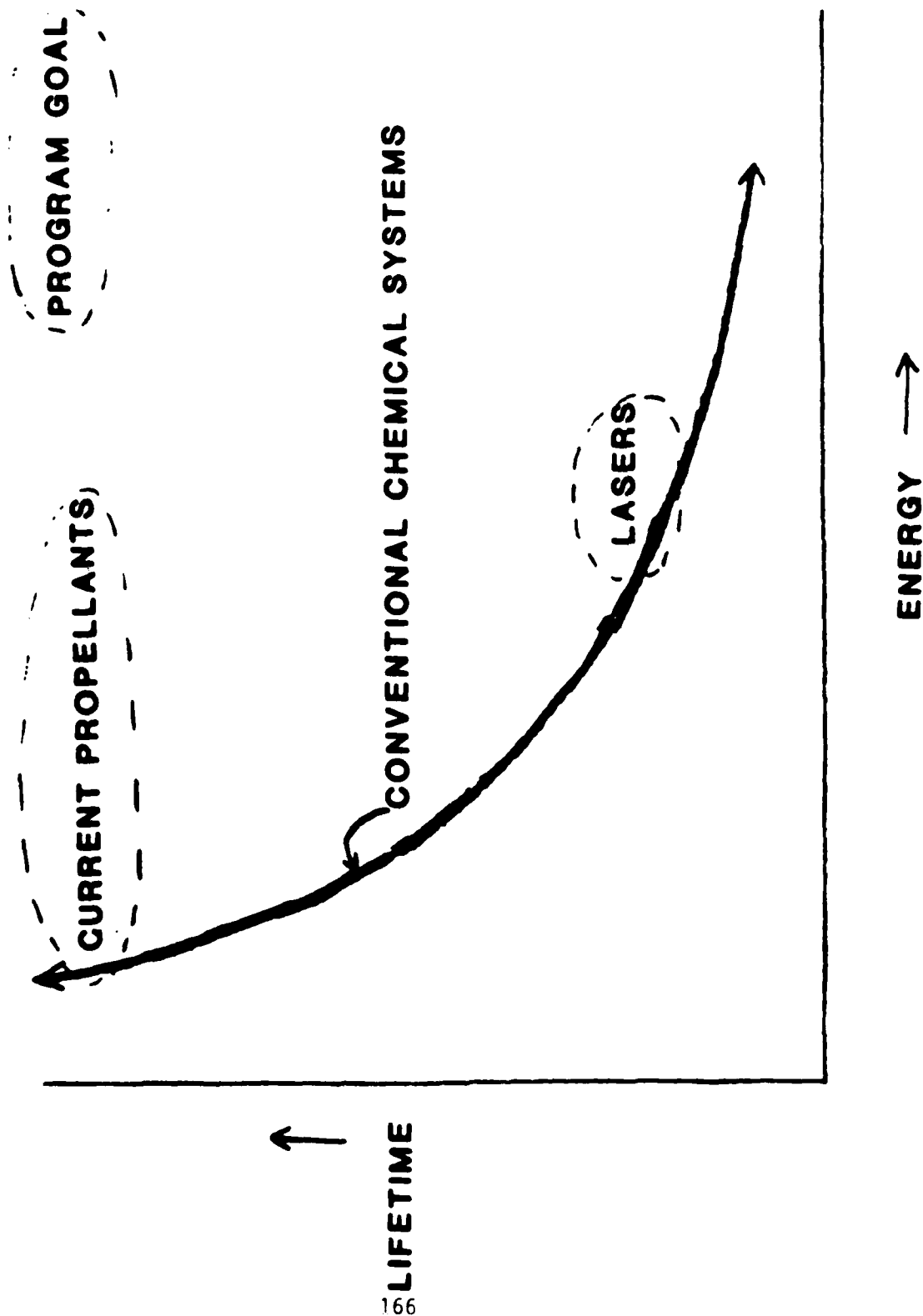
- H_4 STUDIES
- REVOLUTIONARY HIGH ENERGY GROUND STATES
- EVOLUTIONARY SYSTEMS

ELECTRONIC EXCITED STATES

SPIN-ALIGNED SYSTEMS

SURFACE AND MATRIX STORAGE

THE LIMITS OF METASTABILITY



TECHNICAL ISSUES

- **FORMATION MECHANISMS**
- **AMOUNT OF ENERGY STORED**
- **DURATION OF ENERGY STORAGE (LIFETIME)**
- **METHODS OF STABILIZATION AND STORAGE**
- **NOVEL BONDING STRUCTURES**
- **DECAY MECHANISMS**

TECHNICAL SPIN-OFFS

- FUELS
- EXPLOSIVES
- CHEMICAL LASERS
- ENERGY CONVERSION

HIGH ENERGY DENSITY MATERIALS

AFOSR CONTRACTORS

AIR FORCE ASTRONAUTICS LAB - IN-HOUSE PROGRAM

AIR FORCE AERONAUTICS PROPULSION LAB - IN-HOUSE PROGRAM

JOHNS HOPKINS UNIVERSITY - PROFESSOR DAVID YARKONY

SRI - DR HANSPETER HELM

CORNELL - PROFESSORS JOHN WIESENFELD AND BARRY CARPENTER

NBS - DRS MICHAEL CASASSA, JOHN STEPHENSON, AND DAVID KING

NATIONAL HELLENIC INSTITUTE - PROFESSOR C A NICOLAIDES

FUNDAMENTAL STUDIES OF CARBON, NH, AND OXYGEN RINGS

AND OTHER HIGH ENERGY DENSITY MOLECULAR SYSTEMS

PROFESSOR HENRY F SCHAEFER III

UNIVERSITY OF CALIFORNIA, BERKELEY

OBJECTIVE - THEORETICAL INVESTIGATIONS OF STABILITY AND ENERGETICS OF
 $O_N(NH)_N$ AND C_N RINGS

APPROACH - USE HIGH-LEVEL MULTI-REFERENCE CONFIGURATION INTERACTION
AB INITIO MOLECULAR ORBITAL METHODS

1 APRIL 1987 - 30 MARCH 1990 (3 YEARS)

ENERGY FLOW AND DECOMPOSITION OF ENERGETIC
MOLECULES FROM METASTABLE VIBRATIONAL STATES

DRS MICHAEL CASASSA, JOHN STEPHENSON, AND DAVID KING
NATIONAL BUREAU OF STANDARDS
GAITHERSBURG, MD

OBJECTIVE: TO DETERMINE LIFETIMES AND FINAL STATE DISTRIBUTIONS RESULTING
FROM GROUND ELECTRONIC STATE VIBRATIONAL EXCITATION AND DECOMPOSITION OF
ENERGETIC, THERMALLY UNSTABLE MOLECULES

APPROACH: USE TIME-RESOLVED SHORT-PULSE LASER TECHNIQUES TO STUDY E, V, R, T, STATE
DISTRIBUTIONS AND STATE-TO-STATE DECOMPOSITION RATES FOLLOWING DIRECT OVERTONE
EXCITATION OF SMALL ENERGETIC MOLECULES.

1 JANUARY 1987 - 31 DECEMBER 1989 (3 YEARS)

DYNAMIC CONSTRAINTS ON STOCHASTIC BEHAVIOR
IN THE CHEMISTRY OF HIGHLY EXCITED MOLECULES

PROFESSORS BARRY K CARPENTER AND JOHN R WIESENFELD
CORNELL UNIVERSITY
ITHACA, NY

OBJECTIVE: TO DEVELOP A QUANTITATIVE PICTURE OF HIGHLY ENERGETIC CHEMICAL PROCESSES IN ORDER TO CREATE CRITERIA FOR THE EVALUATION OF NEW PROPELLANT SYSTEMS AND THEIR EFFICIENCIES.

APPROACH: DESIGN AND SYNTHESIZE MOLECULES FOR WHICH NON-STOCHASTIC BEHAVIOR IS PREDICTED. COMPARE THE EFFECT OF REGIONAL EXCITATION IN MOLECULES BY LASER OR STORED CHEMICAL ENERGY. DETERMINE IF PREDICTED NON-STOCHASTIC BEHAVIOR IS OBSERVED AND ITS CONSEQUENCES.

15 APRIL 1987 - 14 APRIL 1990 (3 YEARS)

SRI International

Y.K. Bae, P.C. Cosby

Ionic Solid Hydrogen Fuel: Production and Properties of Hydrogen Ion and Energetic Neutral Clusters

Storage of H^{+} H_m^{-} ions in hydrogen matrix

- Production and characterization of H^{+} H_m^{-} ions
- Formation and capture of energetic MIES species
 - Electron capture in hydrogen cluster beam
 - Co-deposition of ionic clusters in H_2 matrix

University of Pennsylvania

W.P. Dailey

Nitrocarbene and Diazirinone Synthesis

Experimental investigation of highly strained nitro compounds

- Lone pair substituted nitrocarbenes
- Organometallic routes to nitrocarbenes
- Synthesis and analysis of diazirinone
- Spectroscopic studies

University of Utah

C.A. Wight

Photoinitiated Chain Reactions in Low Temperature Solids

Experimental Investigation of Cryogenic Solids

- Examine hydrocarbon oxidation reactions
- Examine ignition rates and processes
- Correlate reaction rate to stress fracture propagation

Species

- Cl₂ with hydrocarbons (propane, butane, cyclopropane, ...)
- Seeded hydrocarbons for oxidation reactions
- Diazomethane, hydrozoic acid, or nitromethane for unimolecular reactions

McMaster University

G.J. Schrobilgen

Synthesis and Structural Characterization of New High-Valent Inorganic Fluorine Compounds and their Oxidizing Properties

Synthesis and Preliminary Characterization

- Perfluoro xenon and interhalogen precursors for synthesis
- Substitution reactions to make new xenon, krypton compounds
- Characterize by NMR, IR, mass spec, x-ray crystallography

Species

- O=IF4O- derivatives
- F5TeO- derivatives
- Bromine (VII) oxyfluorides
- Compounds containing a Xe-N bond
- New compound containing first known Xe-C bond

Chemical Physics Institute, Univ of Oregon

P.C. Engelking

Investigations of Hypervalent Compounds as High Energy Materials

Synthesis and Spectroscopy

- Flowing afterglow and cold molecular expansion
- SiH_5^- , CH_5^- , NH_4^-
- Photoelectron and IR spectroscopy
- Photodetachment and photodissociation

Properties

- Thermodynamically or kinetically stable
- Number of equivalent bonds
- Dissociation pathways and barriers
- Geometry and bond constants
- Rigidity of geometry

Louisiana State University

N.E. Brener

Theoretical Studies of Highly Energetic CBES Materials and
Spin Aligned Systems

Theoretical Exploration

- Configuration Interaction (CI) method
- Local density cluster program
- Determine potential energy surfaces and geometries

Species

- Fluorine azide (FN₃) monomer and clusters
- Other CBES materials

University of California, Irvine
V.A. Apkarian

Energy Storage in Condensed Media via Charge Separation and Trapping

- Energy storage by charge separation and ion-hole trapping
- Energy stored until released by thermal shock
- Charge transfer dynamics in RGS of F, Cl, C2
- Other solid matrices include CO, N2, and O2

University of California

C.B. Moore, Y.T. Lee, A.H. Kung
Photochemical Preparation and Spectroscopic
Characterization of H4 and Its Decay Products

-Prepare lowest metastable state of H4 and to determine its stability against radiative decay

- Two approaches:

- 1) prepare on potential surface by single photon excitation
 - 2) prepare on a more highly excited surface by excitation at shorter wavelengths; stimulated emission drops the molecule into the H4 potential well
- Probe decomposition products by laser photoionization and laser induced fluorescence

University of California

W.A. Lester

Quantum Monte Carlo Study of Decomposition Pathways of Tetrahydrogen

- Fixed-node quantum Monte Carlo method to characterize formation and decomposition pathways of tetrahydrogen
- Examine both $\text{H}_3 + \text{H}$ and $\text{H}_2^* + \text{H}_2$ pathways

University of Arizona

P.F. Bernath

Laser and Fourier Transform Spectroscopy of Novel Propellant Molecules

N₃: Fourier transform absorption spectroscopy

Metal Azides: IR laser spectroscopy of LiNN

Metal Nitrides: Near IR spectra of LiN and LiNH

Rydberg Molecules: Fourier transform detection of IR electronic transitions of XeH, NeH, and H₄

Metal Acetylides and Carbides: Visible and IR laser spectroscopy of LiC₂, MgC₂, and LiCCH

HIGH ENERGY DENSITY SYSTEMS IN CRYOGENIC MEDIA
PROF ERIC WEITZ, NORTHWESTERN UNIVERSITY

OBJECTIVE: o DETERMINE DIFFUSION RATES OF SELECTED RADICALS IN SOLID
AND LIQUID MEDIA
o DIFFUSION IS THE MAJOR PROCESS CONTROLLING LOSS OF
CRYOGENICALLY STORED RADICALS

APPROACH: o GENERATE ATOMS AND RADICALS (H, O, F, CL, C₂O, NHX, N₃)
PHOTOLYTICALLY
o DETERMINE REACTION PATHWAYS, RATES AND BRANCHING RATIOS
FOR BOTH GENERATION AND LOSS
o COMPARE REACTIONS IN SOLID VERSUS LIQUID MEDIA
o USE OPTICAL DIAGNOSTICS, INCLUDING TIME RESOLVED INFRARED
ABSORPTION, LIF, FTIR

MEASUREMENT OF THE CHARGE TRANSFER RATE CONSTANT FOR $D_3^+ + SiH_4$

P. D. Haaland and A. Garscadden

Air Force Wright Aeronautical Laboratories

Wright-Patterson Air Force Base

Studies of dissociative charge transfer in silane collisions with SiH_2^+ and SiH_3^+ ions have indicated that H^- is transferred. In silane deposition reactor plasmas, H^+ and H_2^+ also are formed and are expected to rapidly form H_3^+ . The reaction of H_3^+ on silane is therefore of interest. In order to resolve ambiguities in the reaction, the measurements were made using D_3^+ . The experiment utilized a modified Nicolet Fourier Transform Mass Spectrometer. A mixture of deuterium and silane was ionized by an electron beam. The silane ions were then ejected from the trap. The deuterium molecular ions react rapidly with background deuterium to form D_3^+ . The D_3^+ reacts with the background silane to give SiH_3^+ and neutral products. This rate constant is estimated as approximately $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

MEASUREMENT OF THE CHARGE TRANSFER
RATE CONSTANT FOR $D_3^+ + SiH_4$

CAPT PETE HAALAND
ALAN GARSCADDEN

WRIGHT-PATTERSON AFB, OHIO

ABLY ASSISTED BY MR. JIM BARNHART

AD-A187 278

PROCEEDINGS OF THE HIGH ENERGY DENSITY MATTER (HEDM)
CONFERENCE HELD IN R. (U) AIR FORCE ASTRONAUTICS LAB
EDWARDS AFB CA W J LAUDERDALE ET AL. SEP 87

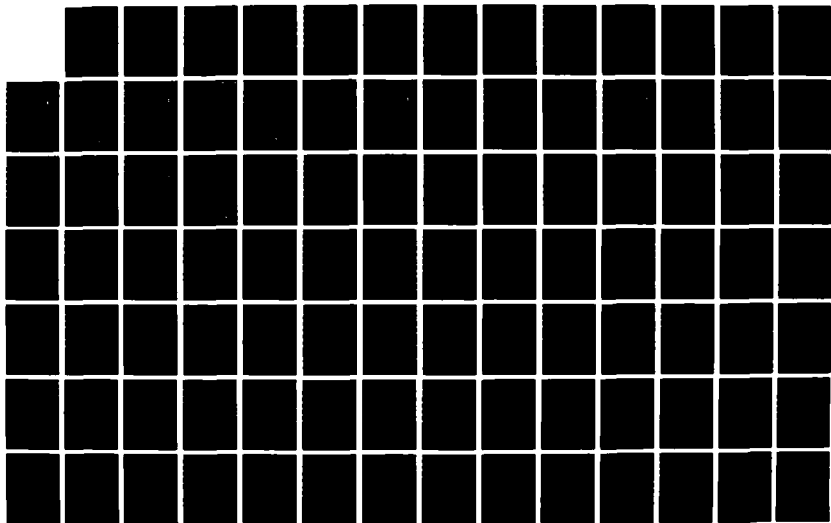
3/5

UNCLASSIFIED

AFAL-CP-87-002

F/G 7/4

NL





H⁻ TRANSFER OBSERVED IN DOUBLE RESONANCE EXPERIMENTS



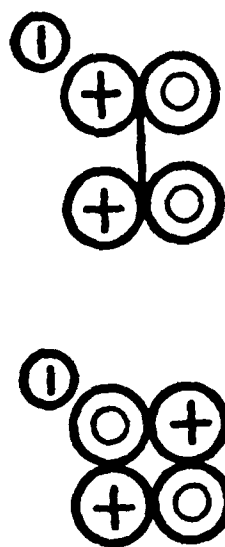
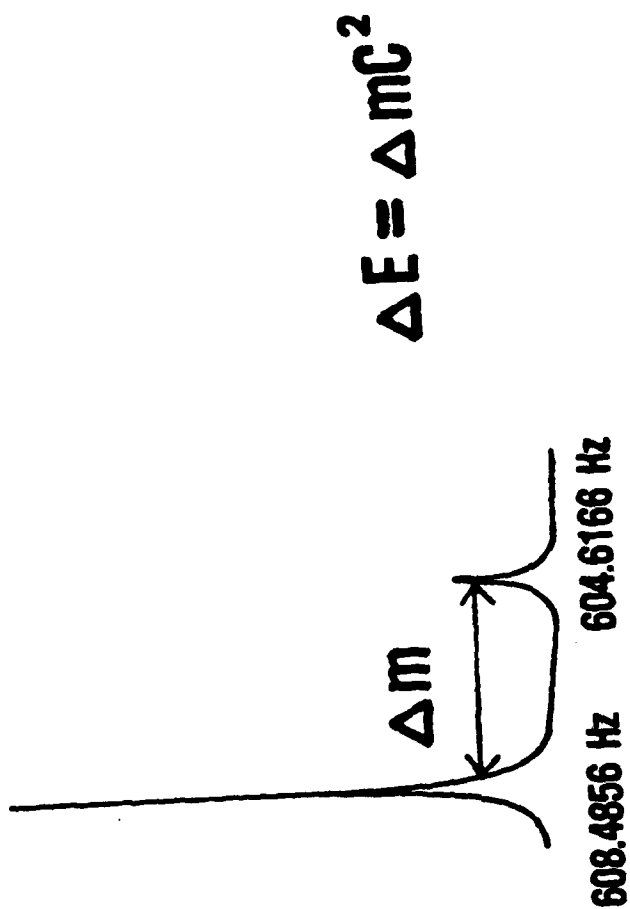
$$k = 1.35 \times 10^{-9} \text{ CM}^3 \text{ SEC}^{-1}$$



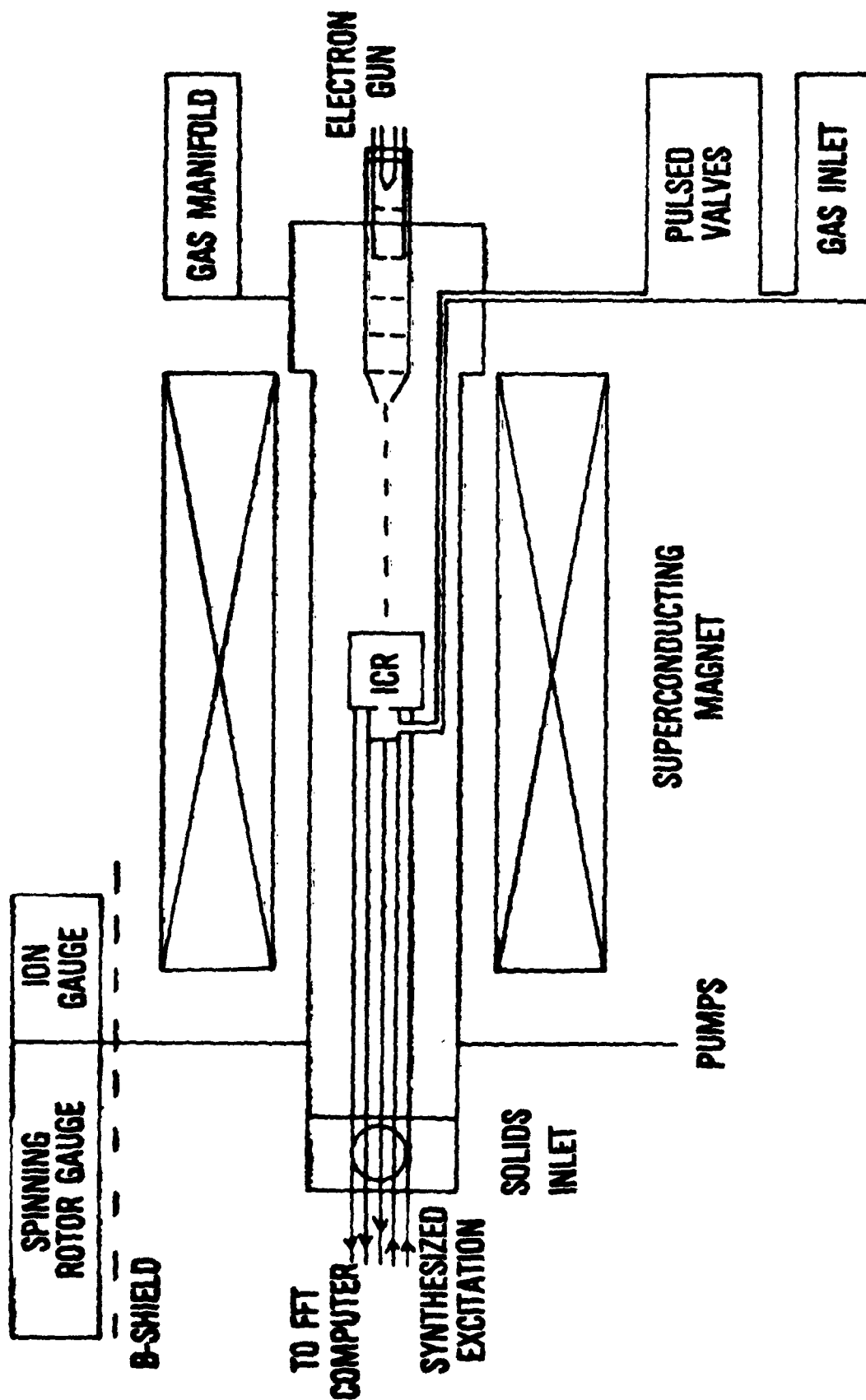
$$k = 1.07 \times 10^{-9} \text{ CM}^3 \text{ SEC}^{-1}$$

HENIS, STEWART, TRIPODI AND GASPAR, J. CHEM. PHYS. 57, 389 (1972)

$\text{He}^+ / \text{D}_2^+$ MASS SPECTRUM



FOURIER TRANSFORM MASS SPECTROMETRY



FOURIER TRANSFORM MASS SPECTROMETRY: UNIQUE FEATURES

- 1. IONS ARE FORMED AND OBSERVED ON TIME SCALES SHORT COMPARED TO THOSE OF PERTURBING REACTIONS**
- 2. IONS ARE FORMED AND DETECTED IN SAME SPATIAL REGION
NO EXTRACTION AMBIGUITIES**
- 3. DETECTED SIGNAL IS LINEAR IN ION NUMBER NO MASS/ENERGY
DEPENDENT FACTORS**
- 4. EXCELLENT SENSITIVITY ($N_j \geq 100$ IONS)**
- 5. VERY HIGH MASS RESOLUTION ($M/\Delta M > 10^6$)**
- 6. EXPERIMENTAL CONFIGURATION ADAPTABLE TO ION SOURCES,
LASER PLASMAS, ELECTRON IONIZATION**

FTMS EXPERIMENT

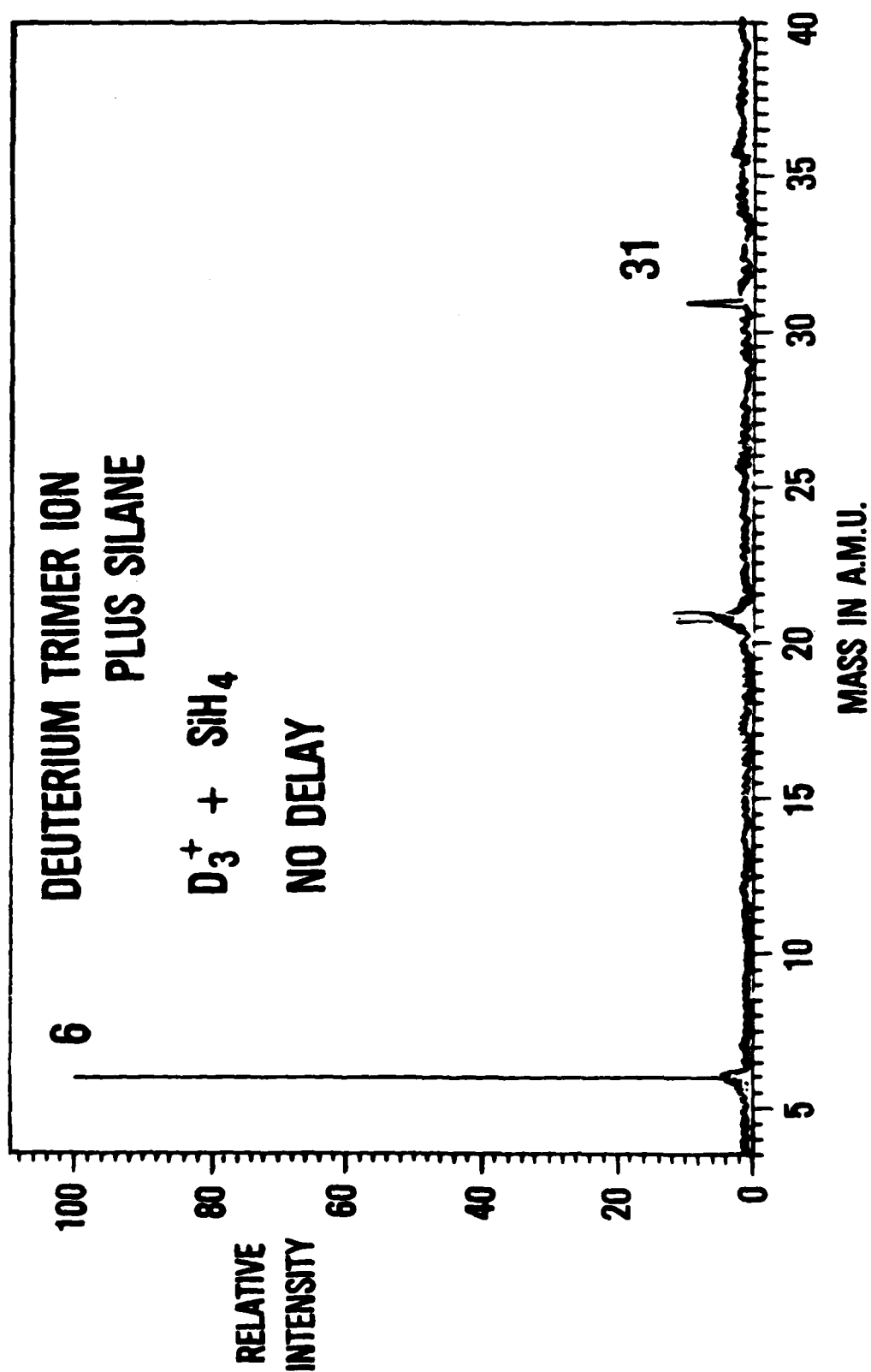
*IONIZE MIXTURE OF DEUTERIUM AND SILANE

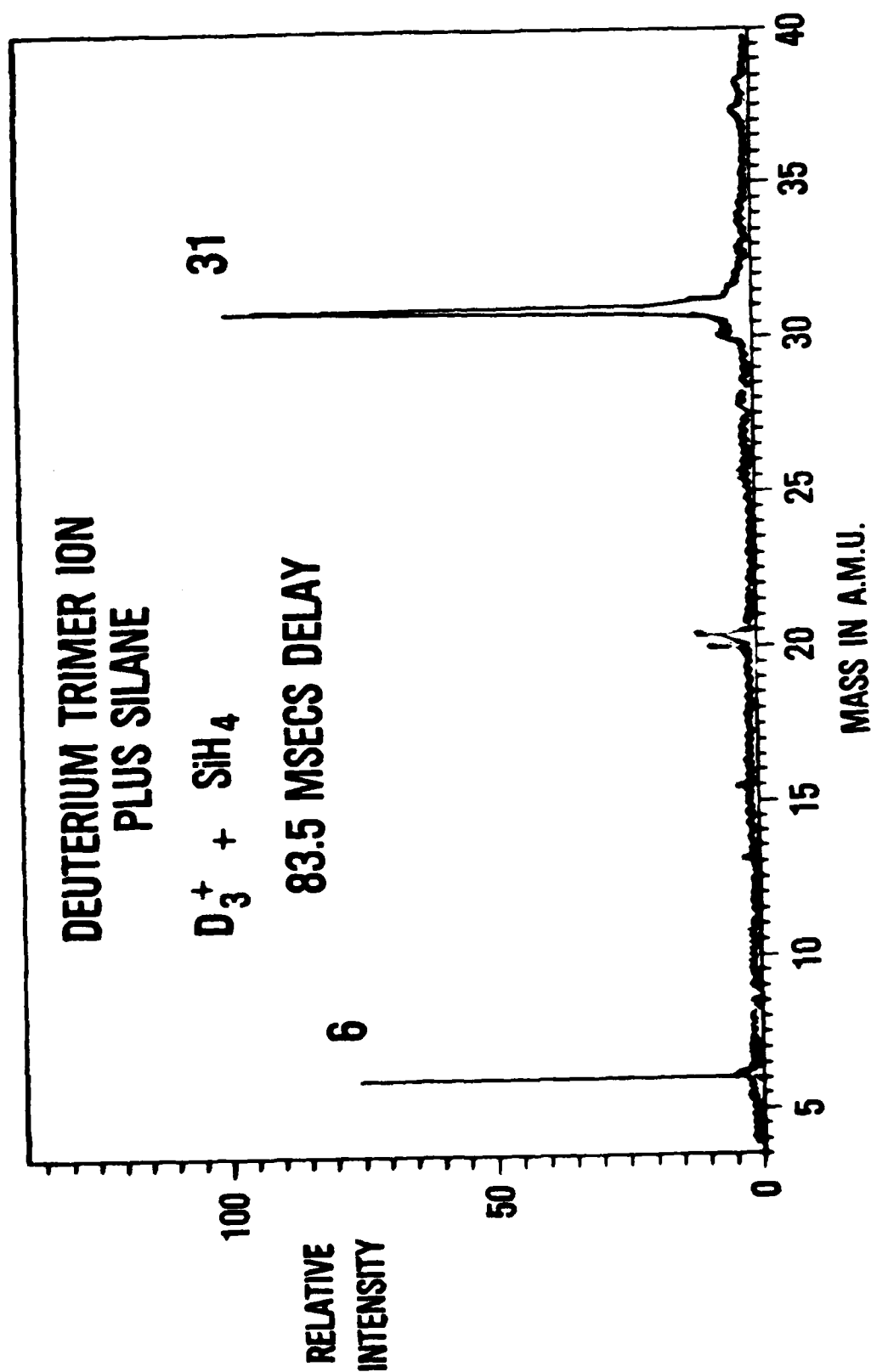
*SWEEP OUT ALL IONS EXCEPT D_2^+

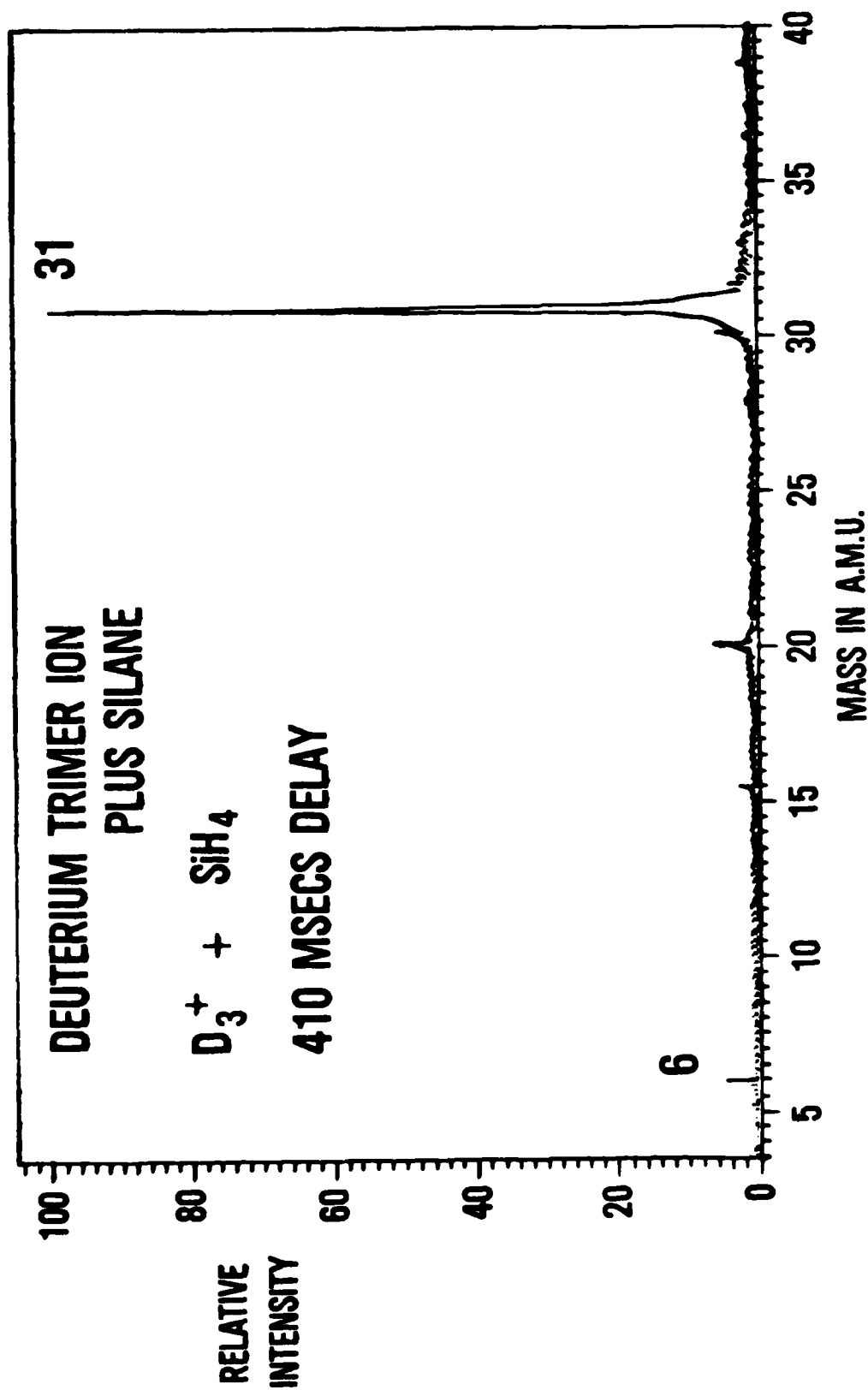
*ALLOW D_2^+ TO REACT WITH D_2

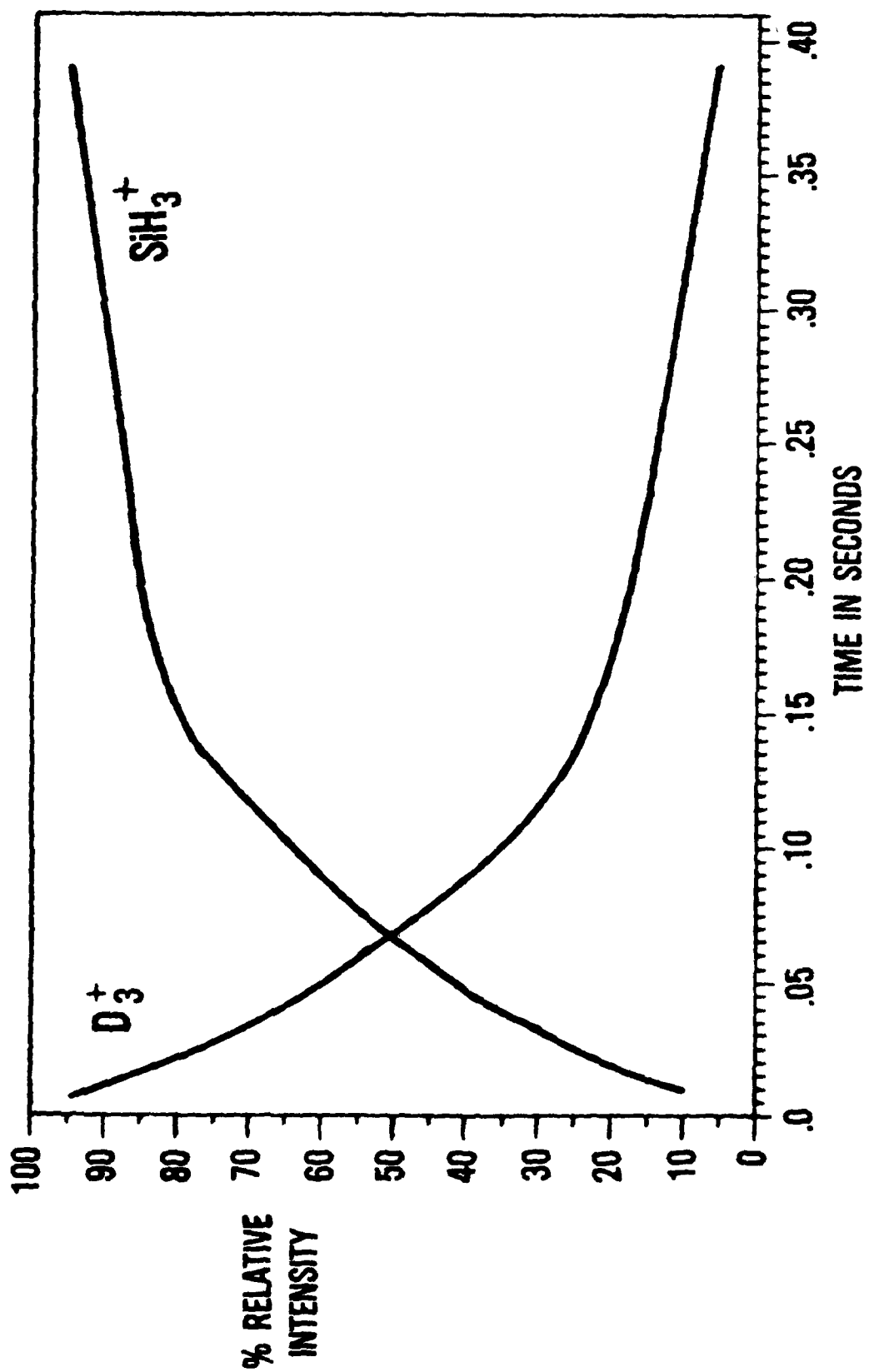
*SWEEP OUT ALL IONS EXCEPT D_3^+

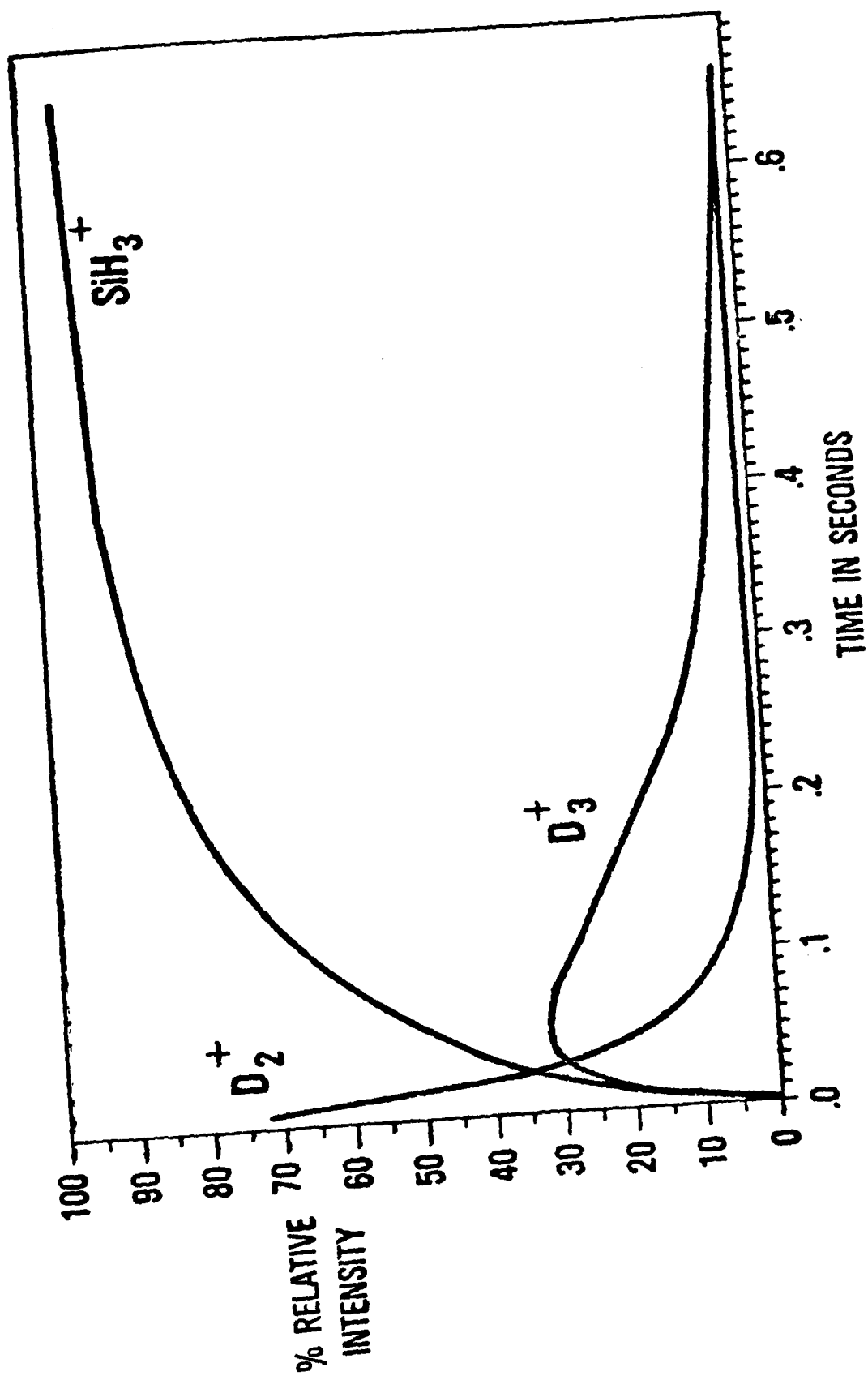
*ALLOW D_3^+ TO REACT WITH SILANE











CONCLUSIONS

- ALTHOUGH He^+ , ELECTRONS AND D_2^+ REACT WITH SILANE TO GIVE Si^+ , SiH^+ , SiH_2^+ AND SiH_3^+ THE REACTION OF D_3^+ GIVES ONLY SiH_3^+
- THE RESULTS OF ALLEN, CHENG AND LAMPE ARE CORRECT: NO SiH_2D^+ IS OBSERVED.
HENCE, $\text{D}_3^+ + \text{SiH}_4 \rightarrow \text{SiH}_3^+ + \text{D}_2 + \text{HD}$ DIRECT H^- TRANSFER
- RATE CONSTANT FOR (2V TRAPPING BIAS) THERMAL IONS $\approx 2.5 \cdot 10^{-9}$
 $\text{CM}^3 \text{ SEC}^{-1}$

EXPLOSIVE DECOMPOSITION OF FLUORINE AZIDE FILMS

D.J. Benard

Rockwell Science Center
1049 Camino dos Rios
Thousand Oaks, CA 91360

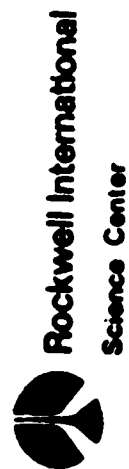
ABSTRACT

The molecule FN_3 , known as fluorine azide, can be viewed as the metastable species $\text{NF}(a^1\Delta)$ bound with N_2 . The nature of the binding will be discussed in terms of the potential surfaces and their correlations to the various excited electronic states of N_2 and NF . Experimental data will also be presented in the form of emission spectra obtained from the laser initiated detonation of thin FN_3 films. These data are expected to shed some new light on methods to stabilize high concentrations of metastable molecules which may be useful as high impulse rocket propellants. The use of FN_3 as a starting material for the generation of high concentrations of $\text{NF}(a^1\Delta)$, to power short wavelength laser systems, will also be discussed.

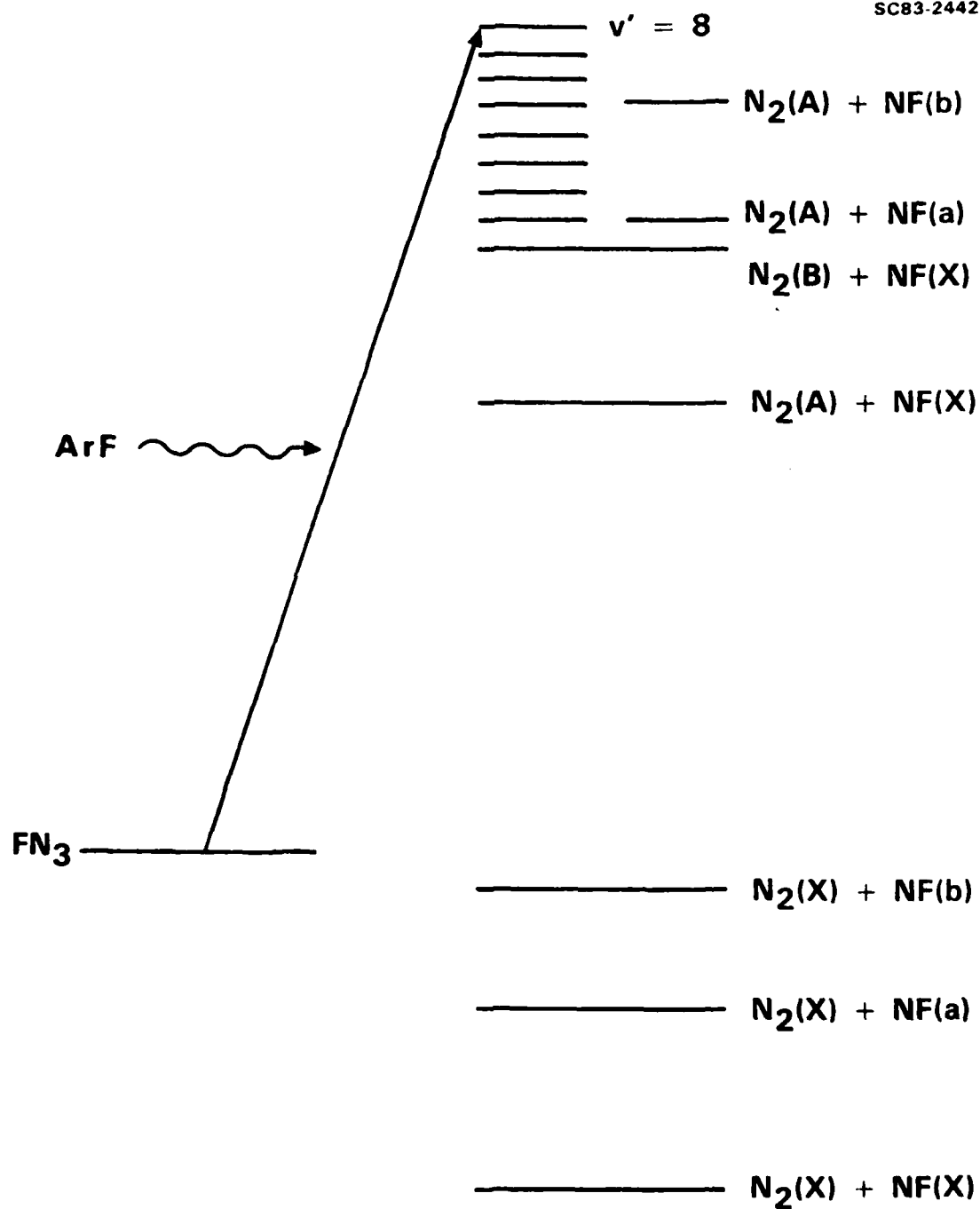
**EVERYTHING YOU EVER WANTED
TO KNOW ABOUT FLUORINE AZIDE ***

D.J. BENARD

*** BUT WERE AFRAID TO ASK**



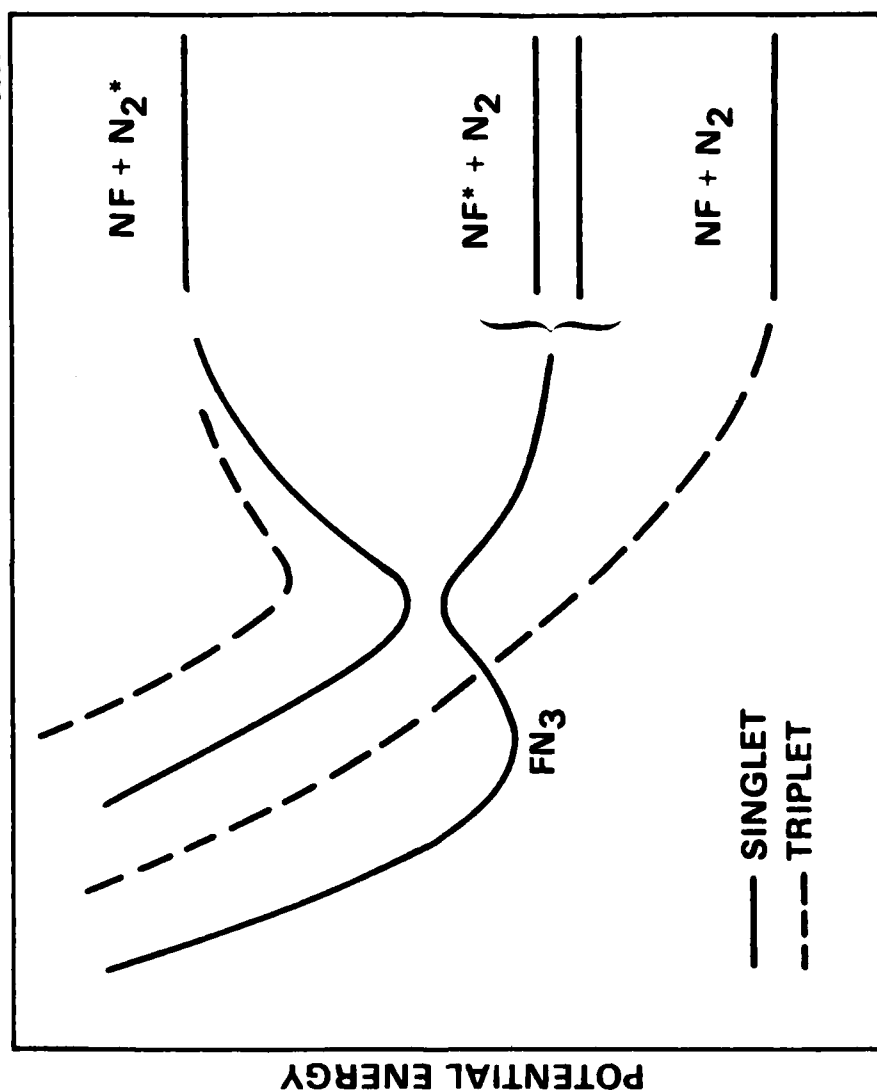
SC83-24423



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POTENTIAL CURVES OF FLUORINE AZIDE

SC39123



FN-N₂ DISTANCE



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FN₃ GROUND STATE CALCULATION

- H. MICHELS, UTRC
 - AB INITIO (SELF CONSISTENT FIELD)
 - HARTREE FOCK SOLUTION, ACCURACY 10 - 20%
- VIBRATIONAL FREQUENCIES (CM⁻¹)

	<u>CALCULATED</u>	<u>MEASURED</u>	<u>MODE</u>
V ₁	281	241	BENDING
V ₂	606	504	BENDING
V ₃	757	658	SYM. N ₃
V ₄	1045	874	NF STRETCH
V ₅	1225	1090	ASYM. N ₃
V ₆	2386	2037	N ₂ STRETCH

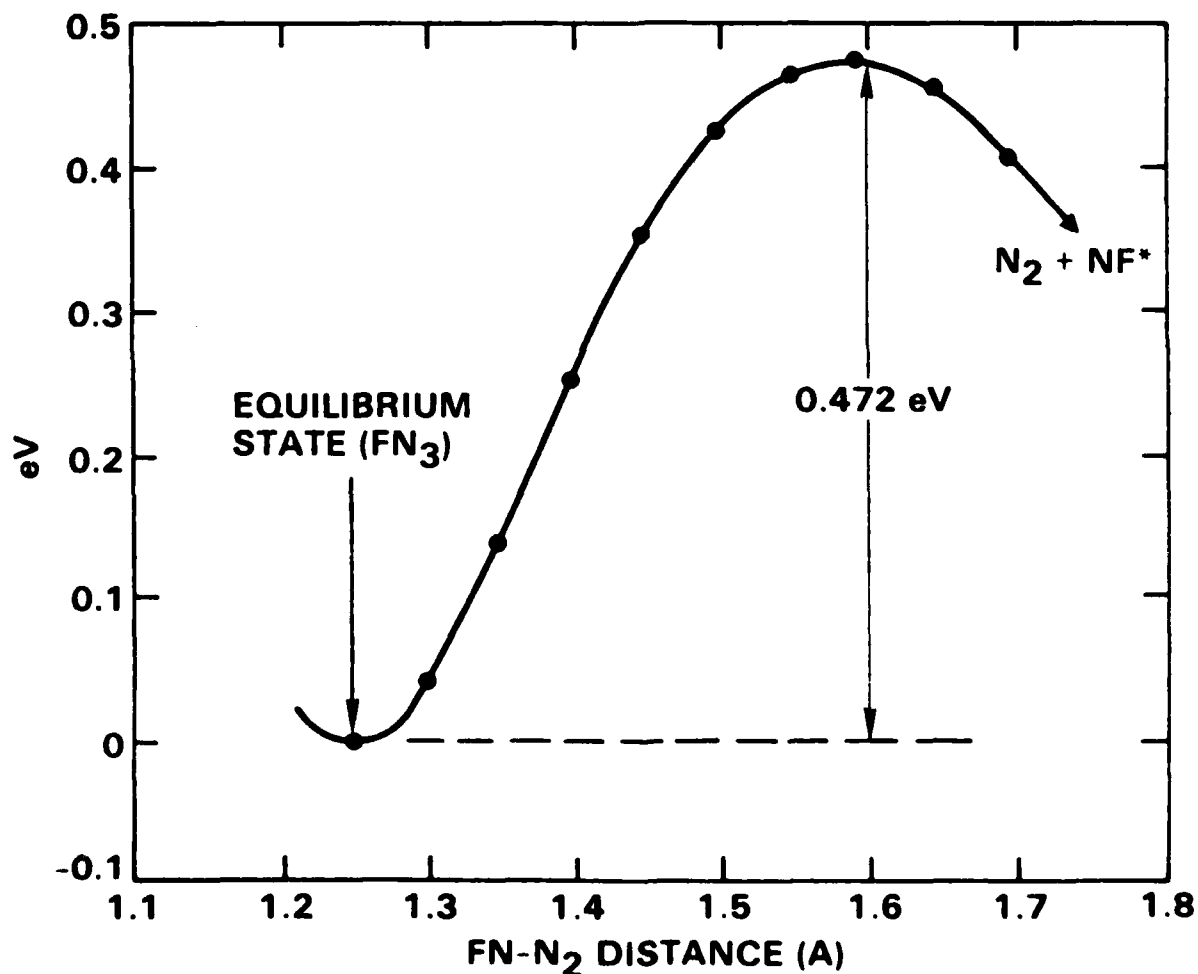


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DISTORTED MOLECULE CALCULATION

SC39126

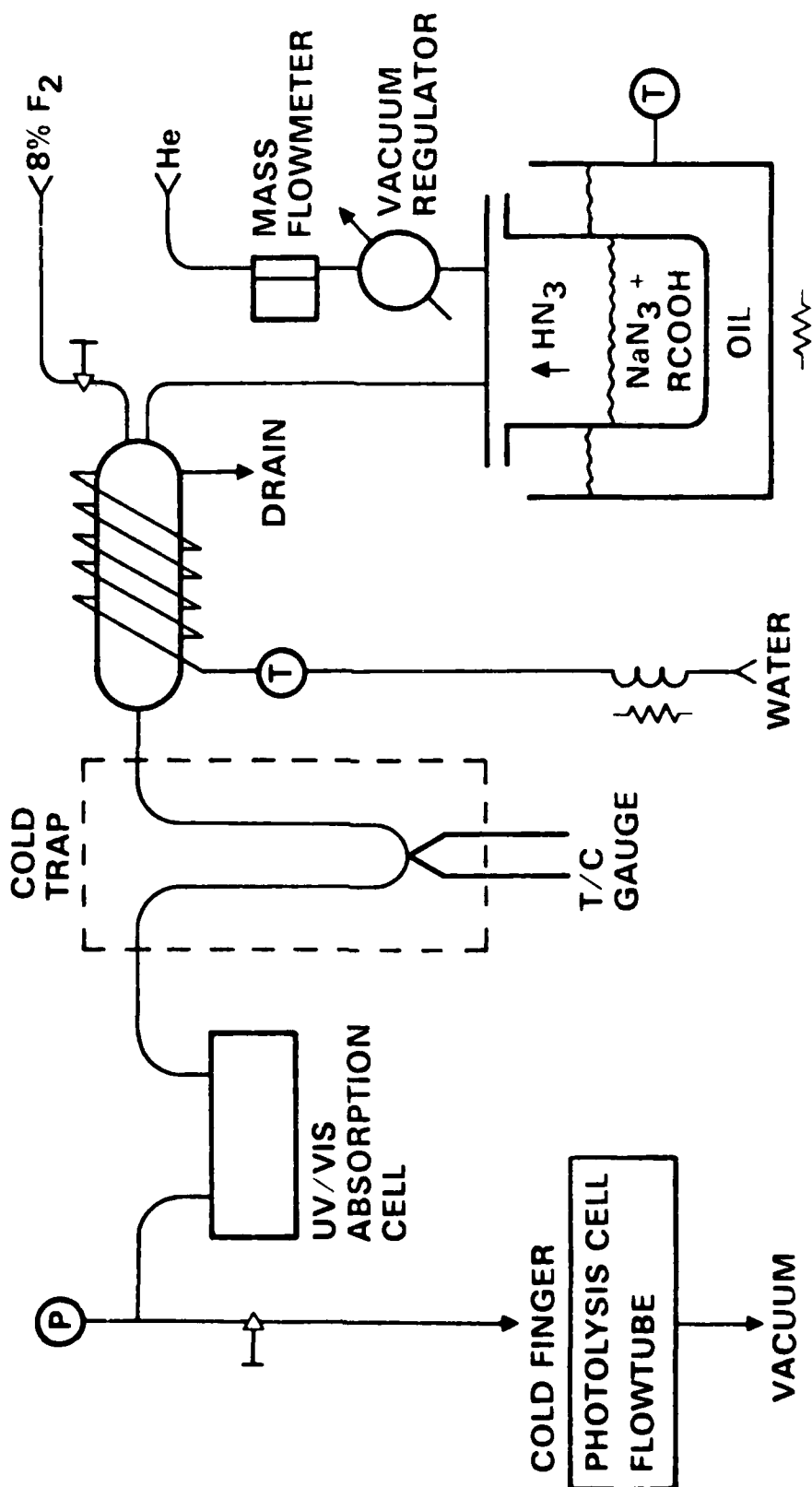
- FN-N₂ BOND SPECIFIED (GROUND STATE)
- F-N₃, FN₂-N BONDS OPTIMIZED (3-D)
- LOWEST CHANNEL (CONSERVED SPIN)



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FN₃ RESEARCH FACILITY

SC39118

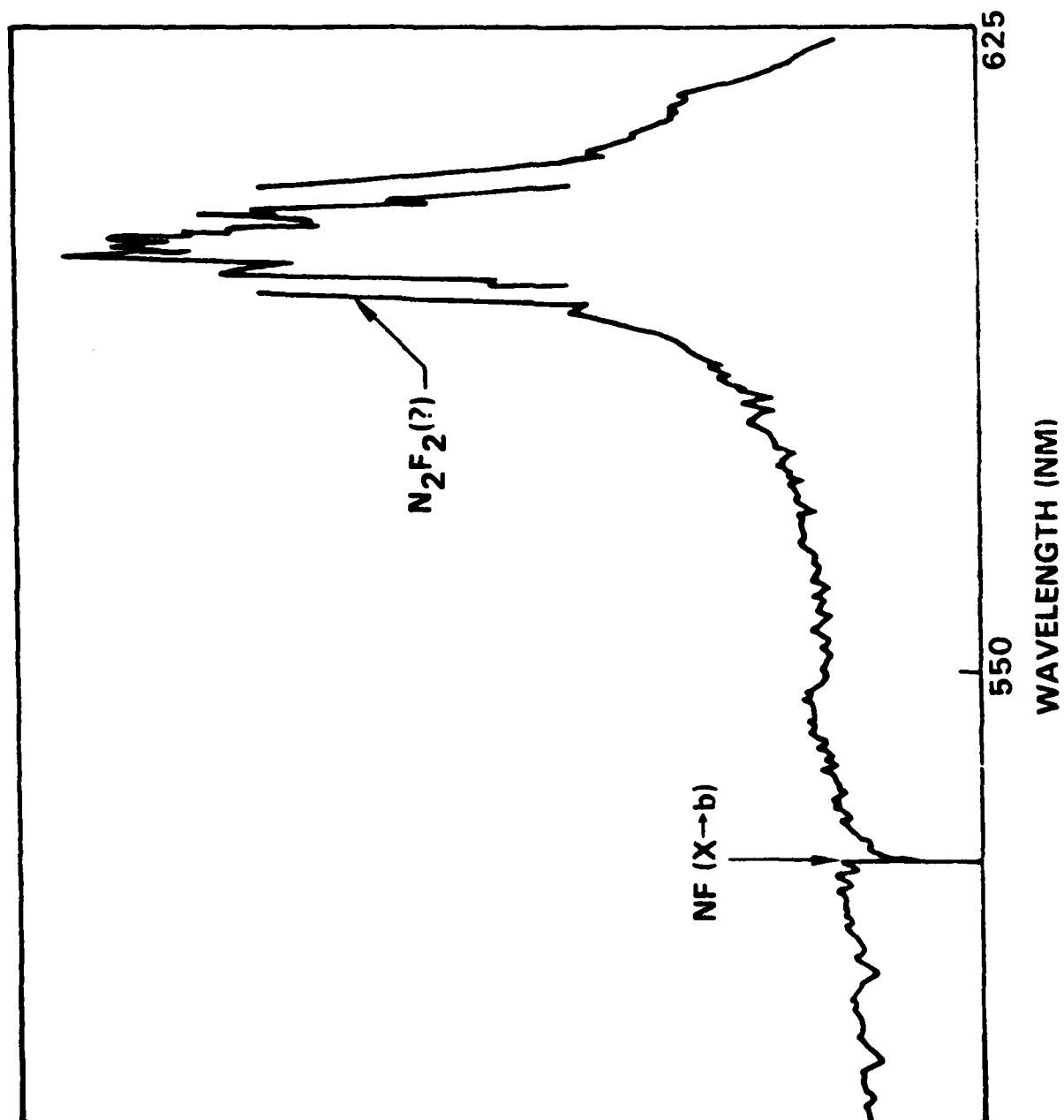


AFRPL CONTRACT

- RATIONALE: FN_3 MODELS H_4
- APPROACH:
 - PRODUCE FN_3 IN GAS STREAM
 - CONDENSE ONTO COLD FINGER
 - DETONATE
 - ANALYZE EMISSION / ABSORPTION DATA
 - SPECTROSCOPY
 - KINETICS
- OBJECT: STABILIZATION METHODS

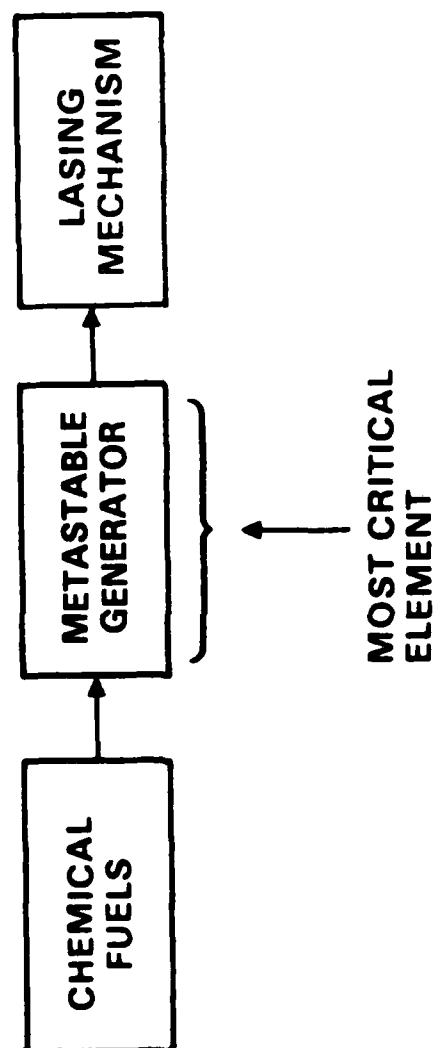


SC40133



KEY ELEMENTS OF SWCL

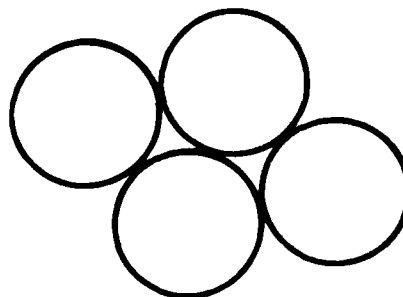
SC39117



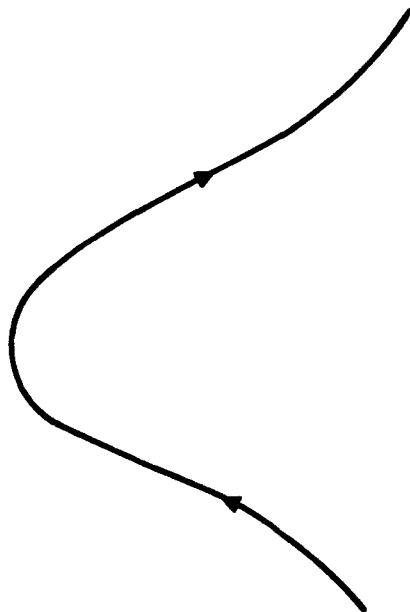
ALTERNATIVE GENERATION SCHEME

SC39125

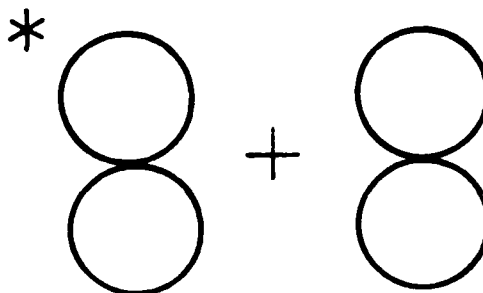
ENERGETIC
MOLECULE



POTENTIAL
BARRIER



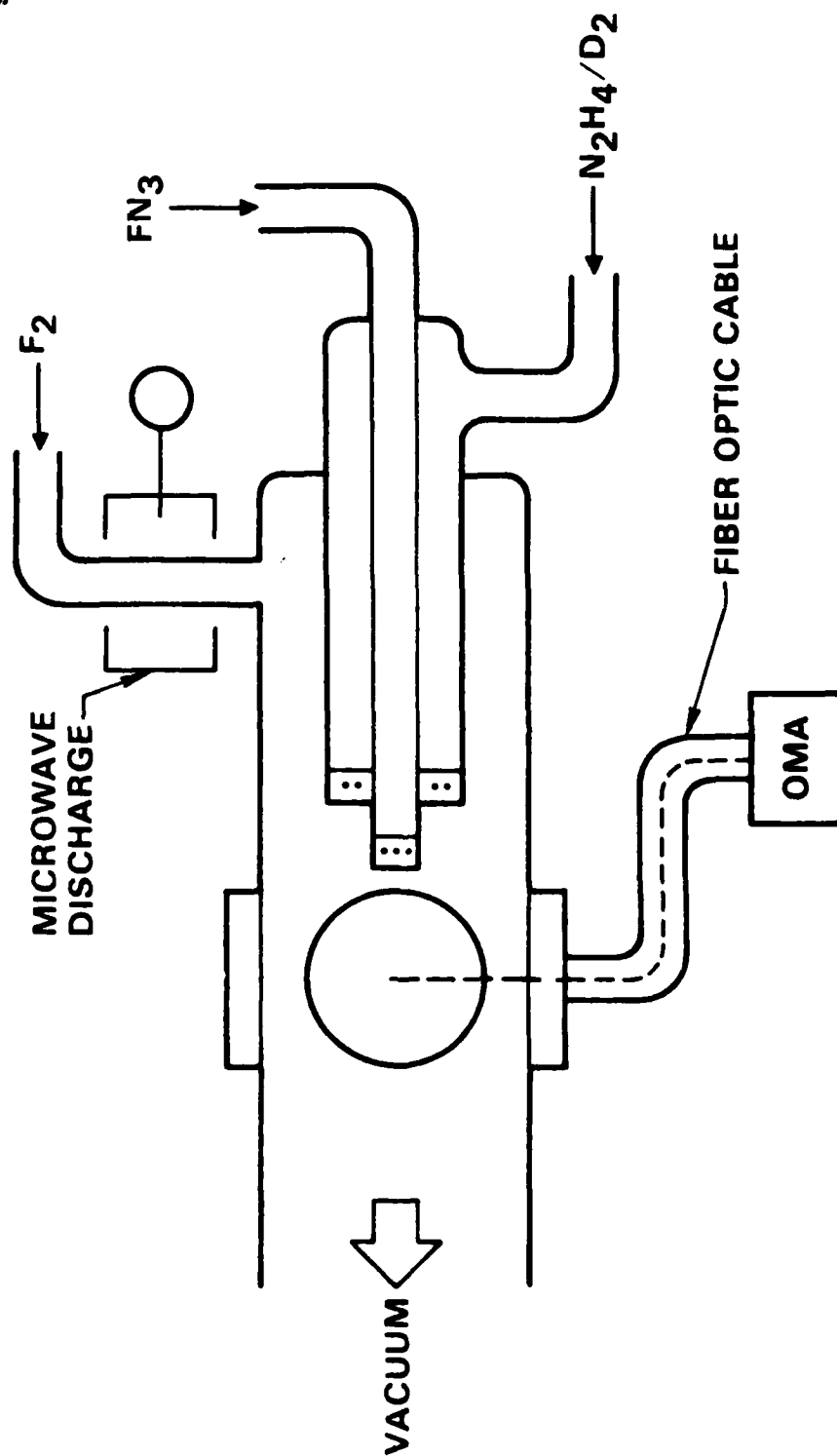
EXCITED
PRODUCTS



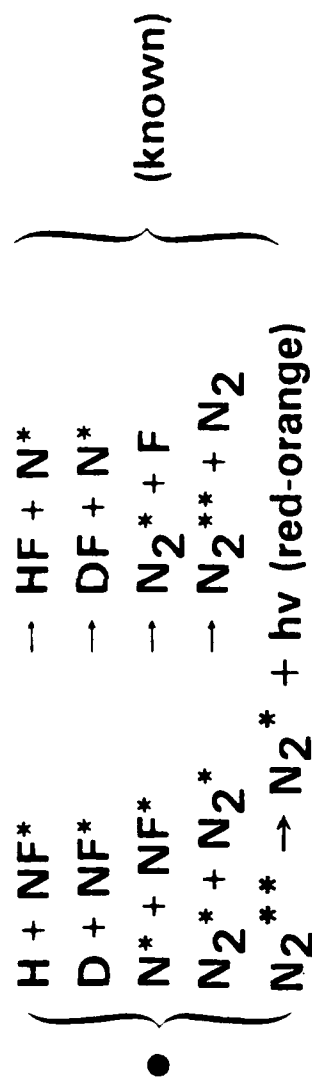
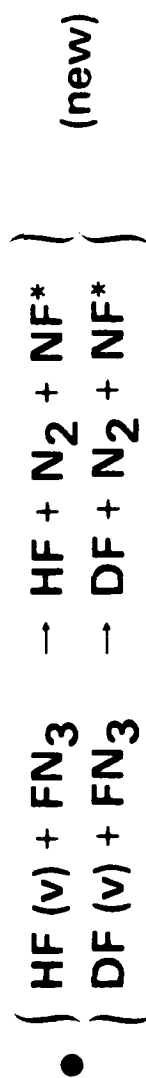
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FLOWTUBE EXPERIMENT

SC39120

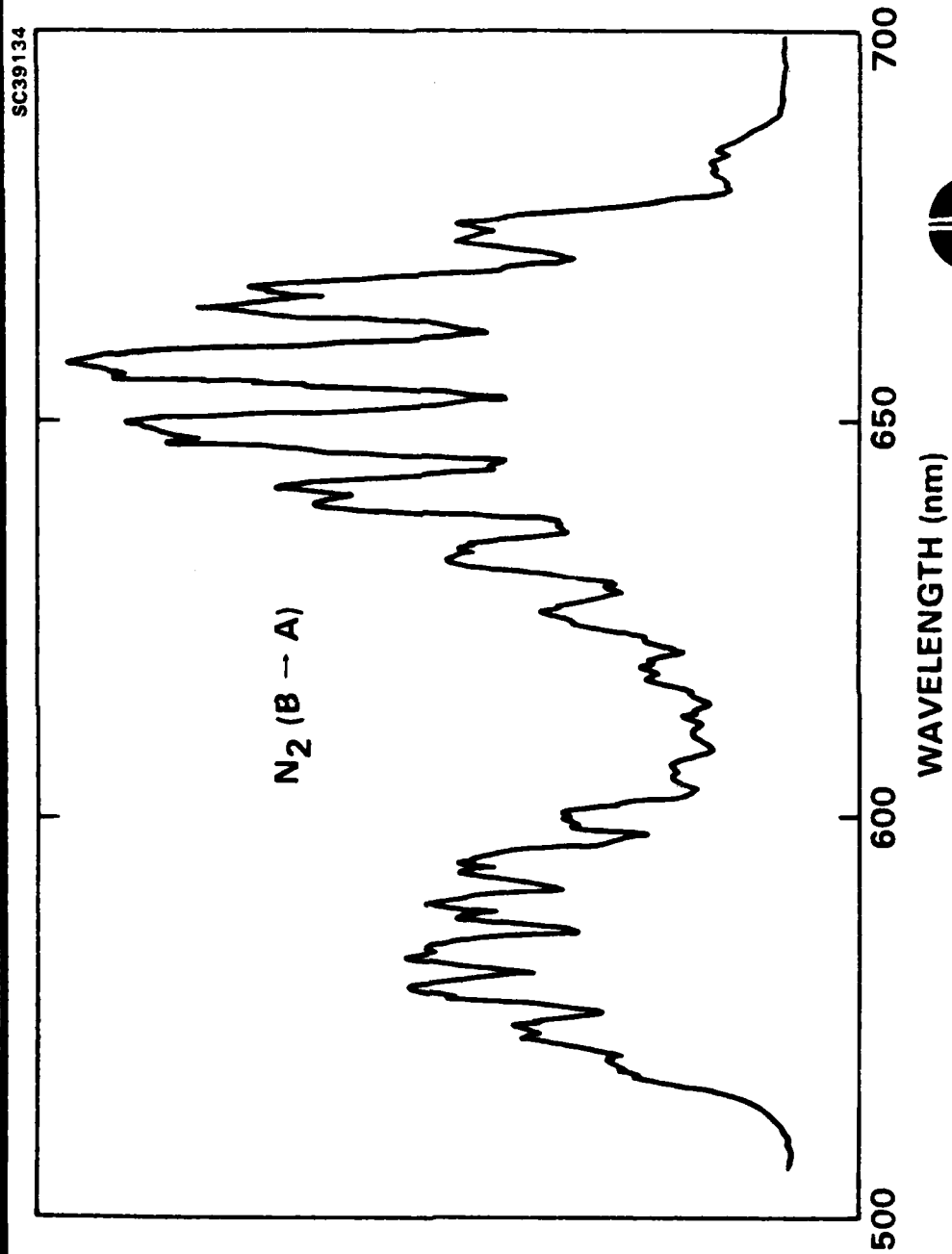


KEY REACTION STEPS

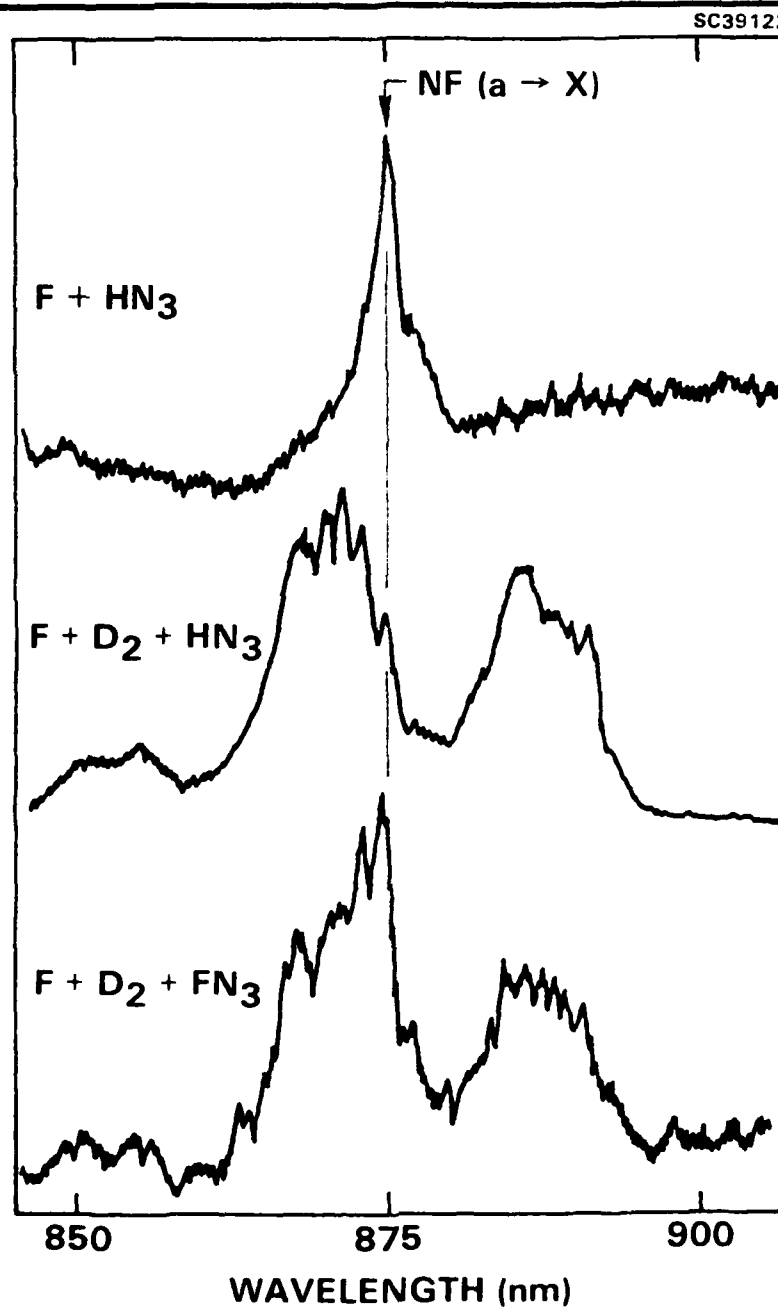


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VISIBLE F + D₂ + FN₃ CHEMILUMINESCENCE

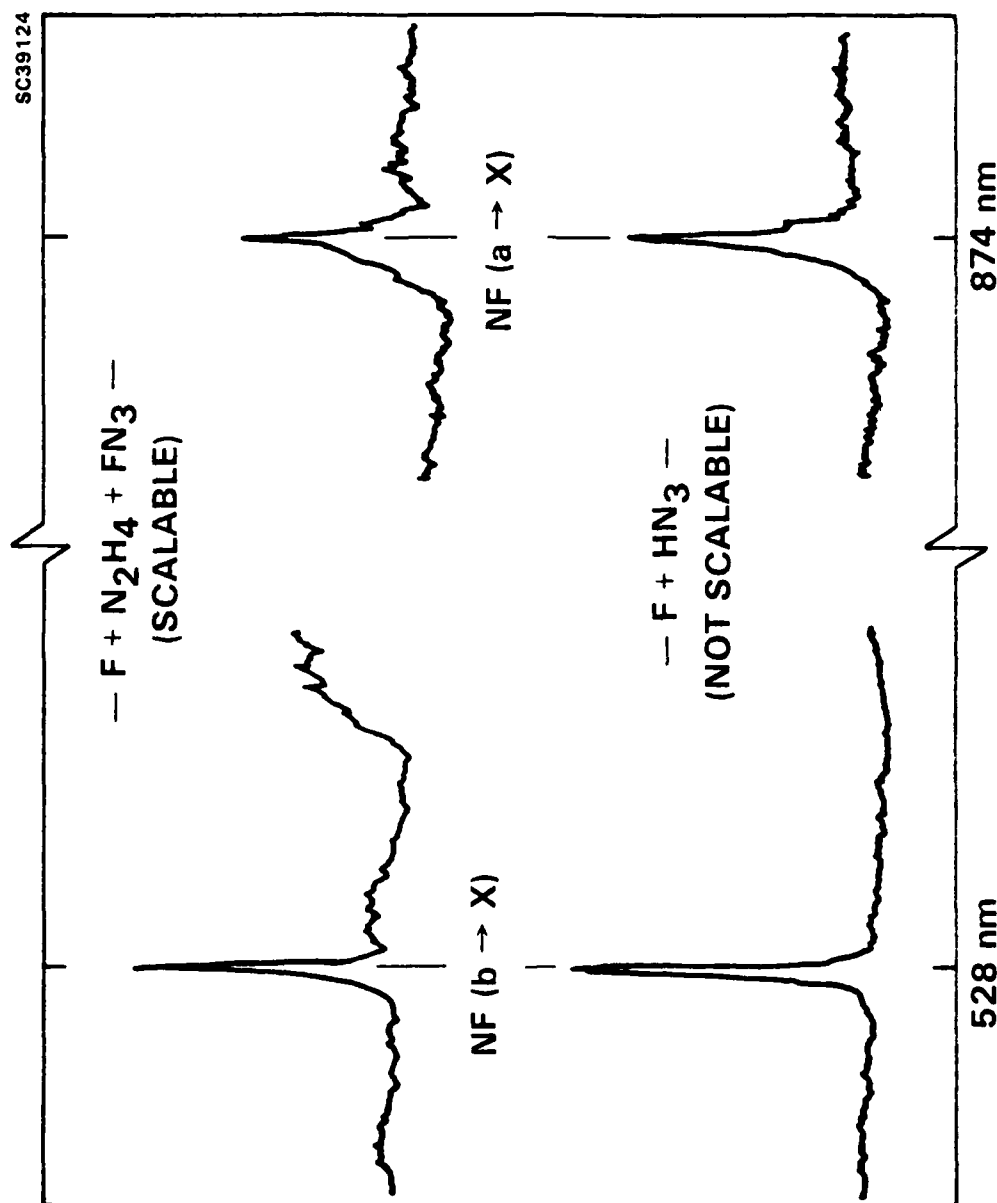


NEAR IR FLOWTUBE CHEMILUMINESCENCE



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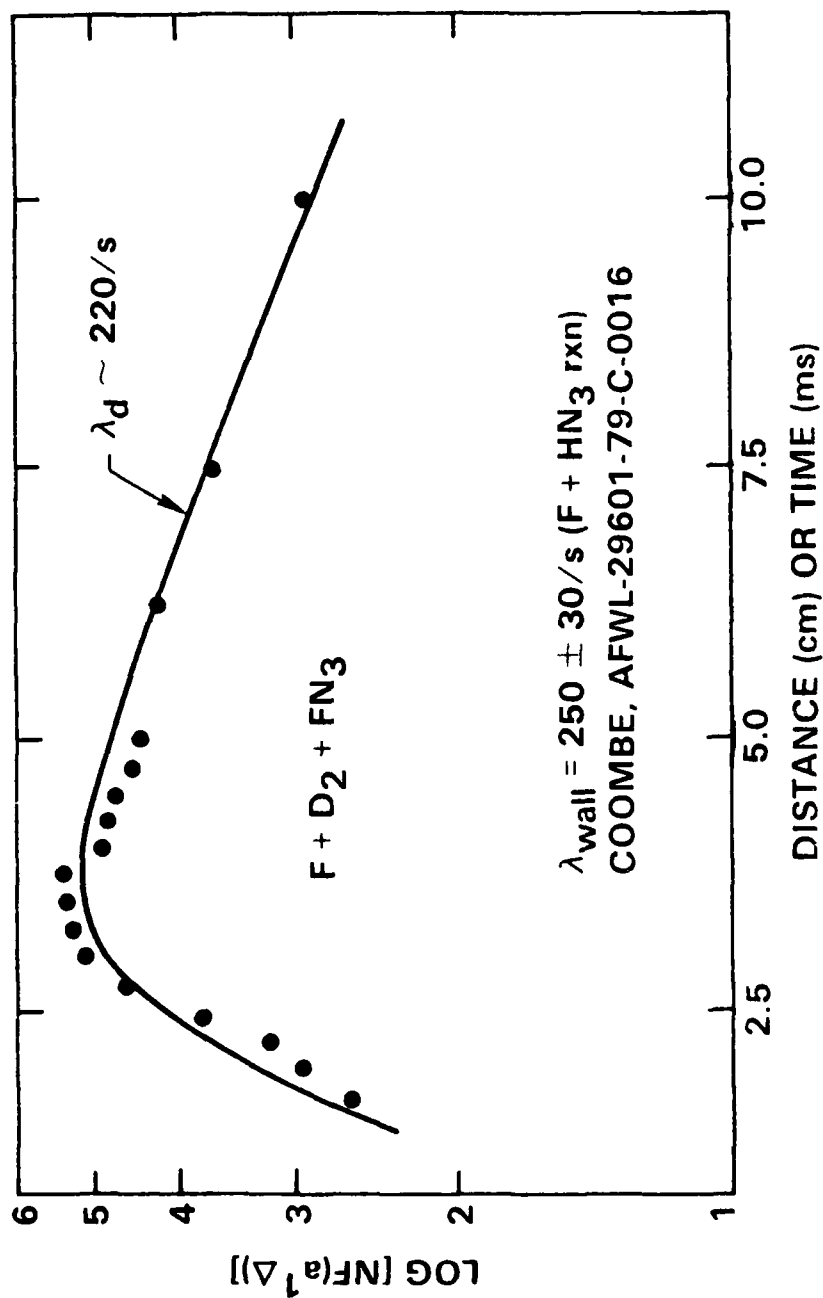
CHEMILUMINESCENCE COMPARISON



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SLOW DECAY OF NF ($a^1\Delta$)

SC39135



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CONCLUSIONS

- FN3 IS A LOOSELY BOUND COMPLEX OF EXCITED SINGLET NF AND N2.
- BARRIER HEIGHT TO DISSOCIATION IS APPROXIMATELY 0.5 EV.
- ENERGY TRANSFER FROM HF/DF(v) TO FN3 IS AN EFFICIENT SOURCE OF EXCITED NF.



ELECTRONIC STRUCTURE AND STABILITY OF ENERGETIC CHEMICAL SPECIES

**H.H. Michels
J.A. Montgomery, Jr.**

**Presented at
AFRPL / HEDM Conference
Rosslyn, Va
May 12 - 13, 1987**



RF1130TX.006

Electronic Structure and Stability of Energetic Chemical Species

H. H. Michels and J. A. Montgomery, Jr.
United Technologies Research Center
East Hartford, CT 06108

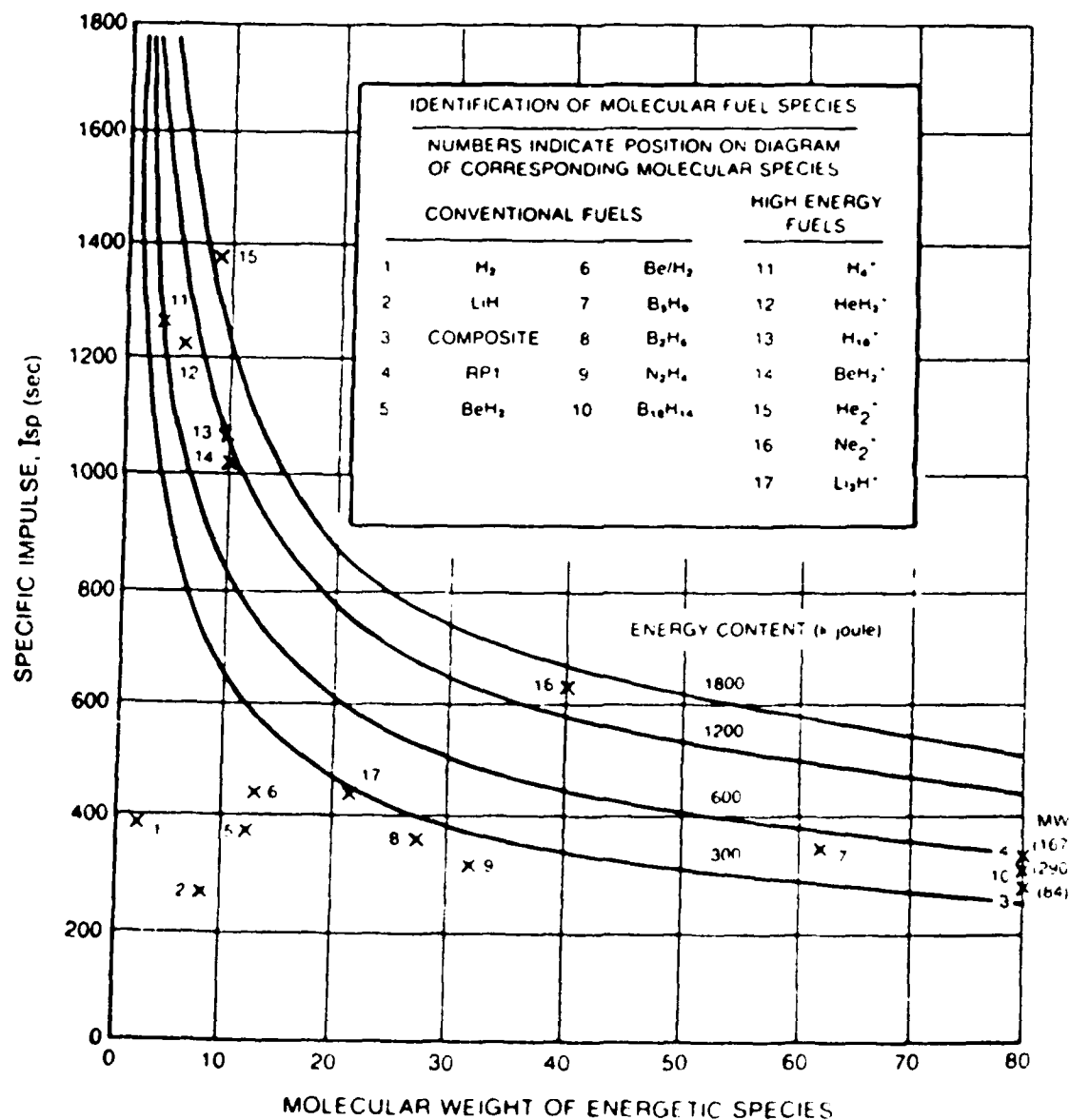
ABSTRACT

Theoretical quantum mechanical calculations have been carried out for several potentially high energy chemical species. Our research objectives are to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems. A parametric study of the deliverable specific impulse as a function of available reaction energy and propellant weight indicates that primary consideration should be given to molecular structures that can be formed from hydrogen through boron and that have a molecular weight of 40 or less.

Calculations to date have been performed on three classes of light element compounds: C_{3v} structures such as H_4 and Li_3H , azide structures such as N_3F and αN_2O_2 and cyclic boron structures such as B_3H_3 and B_2H_2NH . We find that the ground state potential energy minimum found for H_4 in C_{3v} symmetry corresponds to a saddle region rather than a stable bound state and that distortion via vibrational or rotational modes leads monotonically to dissociation into two H_2 molecules. In contrast, Li_3H appears to be chemically stable in C_{3v} symmetry. Our studies of asymmetric dinitrogen dioxide (αN_2O_2) indicate a stable azide-like structure in C_s symmetry for the ground $^1A'$ state, with an indicated heat of formation of +430 kJoule/mol. This molecule is a very attractive candidate as an advanced oxidizer. Our preliminary calculations for boron compounds indicate that B_3H_3 is unstable in D_{3h} symmetry but that iminodiborane (B_2H_2NH) is stable in C_{2v} symmetry. The electronic structure, vibrational analysis and thermodynamic stability of these compounds will be described.

SPECIFIC IMPULSE OBTAINABLE FROM FUEL/OXIDANT ENERGY RELEASE WITH HYDROGEN AS A WORKING FLUID

HYDROGEN CONTENT VARIED TO OPTIMIZE IMPULSE (1000-14.7 psia)



CATEGORIES OF ENERGETIC SPECIES

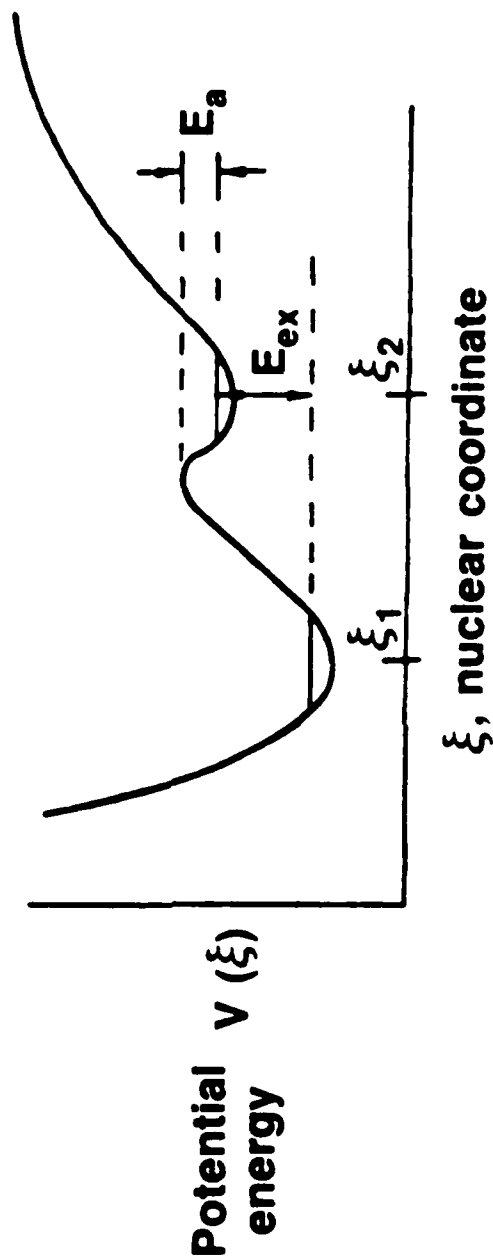
- 1) Ordered (or metallic) forms of matter which at conventional temperatures and pressures are molecular solids. Metallic hydrogen and ammonium are examples.

- 2) Free radicals, either atomic or molecular in nature, that are stabilized against recombination by condensation and immobilization on noble gas matrices held at very low (4 K) temperatures. Atomic hydrogen, beryllium monohydride (BeH) and the hydroxyl (OH) radical are examples in this category.

- 3) Electronically excited metastable atoms or molecules that are stabilized against radiative decay by externally applied electric, magnetic or radiation fields, or by an intrinsic field within a condensed phase of such material which acts as a barrier to their decay. Metastable atoms, such as $\text{He}^*(^3\text{S})$ or $\text{N}^*(^2\text{D})$, and metastable molecules, such as $\text{He}_2^*(\text{a}^3\Sigma_u^+ \text{ or } ^5\Sigma_g^+)$, $\text{HeH}_2^*(^1\text{A II})$ and $\text{H}_2^*(\text{B}^1\Sigma_u^+)$, are examples in this category that would constitute significant energy sources ($> 1000 \text{ kJoule/mol!}$). Other energetic metastable species such as $\text{O}_2(\text{a}^1\Delta\text{g})$, $\text{NF}(\text{a}^1\Delta)$ and $\text{Mg}^*(^3\text{P})$, with long radiative lifetimes, may also be useful as temporary energy storage media.

- 4) Strained molecules with high positive heats of formation. This is an important class of molecules which are really isomeric forms of conventional chemical species but are structurally prevented from relaxation to their lowest energy state by significant activation barriers on their potential energy surface. Examples in this category include cyclopropylene (C_3H_4), aziridine ($\text{C}_2\text{H}_2\text{NH}$), azetidine ($\text{C}_3\text{H}_3\text{NH}$), hydrogen azide (HN_3) and fluorine azide (FN_3).

HIGH ENERGY MOLECULAR CONFORMATION



TYPES OF COMPOUNDS STUDIED TO DATE

A. Light element C_{3v} structures

H_4 , LiH_3 , Li_3H , Li_4

B. Azide structures

FN_3 , $FNCO$, $a-N_2O_2$, $FNBF$

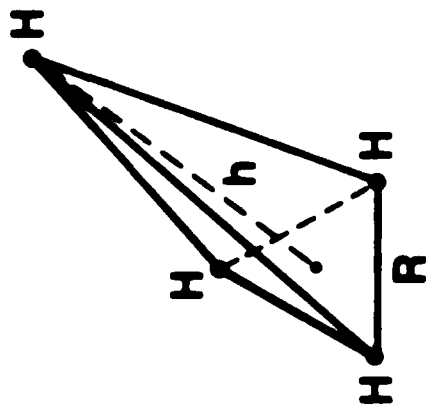
C. Cyclic boron structures

B_3H_3 cyclotriborane

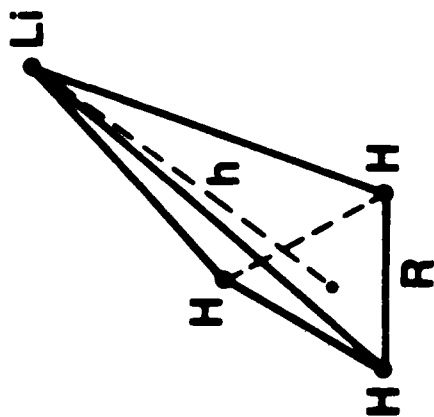
B_2H_2NH iminodiborane

NF11307X 005

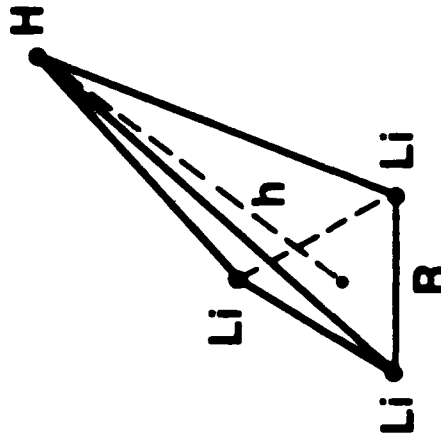
A. HIGH-ENERGY LIGHT ELEMENT MOLECULAR STRUCTURES



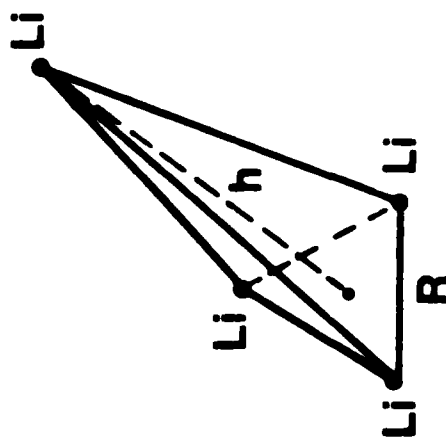
a) H_4 (C_{3v})



b) LiH_3 (C_{3v})



c) Li_3H (C_{3v})



d) Li_4 (C_{3v})

H₄(C_{3v}) CALCULATIONS

Theory	h	r	Energy	Frequencies		
				e	a ₁	e
SCF / small	1.8784	0.8433	-1.982 831	2942i	1053	3069 3794
MP2 / small	1.8094	0.8477	-2.035 124	3614i	1096	3010 3751
CISD / small	1.8048	0.8509	-2.049 161	4025i	1092	2962 3712
SCF / large	1.8634	0.8421	-2.000 761	2188i	1167	3101 3777
MP2 / large	1.8170	0.8451	-2.063 595	2503i	1201	3051 3740

Energies (hartrees), distances (Å), frequencies (cm⁻¹)

Li₃H CALCULATIONS

Theory	h	r	Energy	Frequencies		
				e	a ₁	a ₁
SCF/3-21G	1.1634	2.6564	-22.709865	277	400	407 836
SCF/3-21G**	1.1629	2.6497	-22.710567	280	400	401 848
MP2/3-21G**	1.1091	2.6644	-22.752360	268	518	384 835
SCF/6-31G*	1.1992	2.6461	-22.857226	247	344	400 821
SCF/6-31++G*	1.1895	2.6563	-22.859319	258	349	389 809
SCF/6-311G**	1.1422	2.5993	-22.867477	291	421	390 837

Energies (hartrees), distances (Å), frequencies (cm⁻¹)

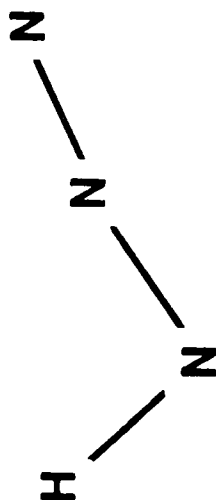
LiH₃ AND Li₄ CALCULATIONS

Theory	h	r	Energy	Frequencies			
				e	a ₁	e	a ₁
<u>Li₄</u>							
SCF/3-21G	3.1300	2.8191	-29.529616	218i	193	285	356
SCF/3-21+G	3.1304	2.8205	-29.530374	214i	192	284	354
SCF/6-31G*	3.1439	2.8193	-29.722764	239i	199	281	351
SCF/6-31+G*	3.1526	2.8257	-29.724402	225i	195	280	349
<u>LiH₃</u>							
SCF/3-21G**	1.5967	1.2216	-8.832136	Unstable (2)			
SCF/6-31G**	1.5954	1.2294	-8.887511	Unstable (2)			

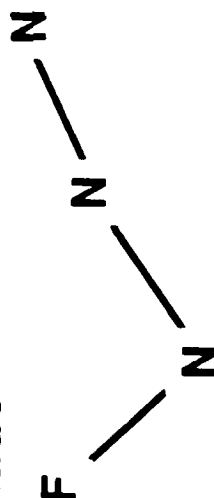
Energies (hartrees), distances (Å), frequencies (cm⁻¹)

B. AZIDE-TYPE STRUCTURES

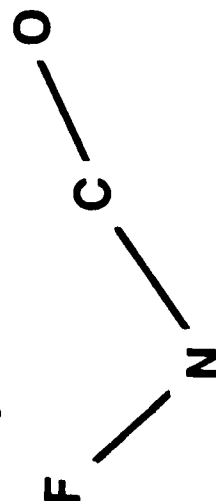
Hydrogen azide



Fluorine azide



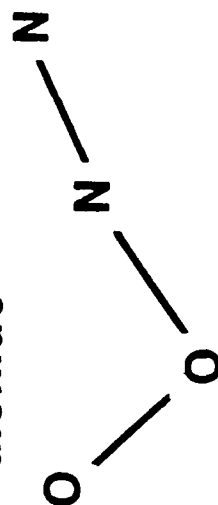
Fluorine isocyanate



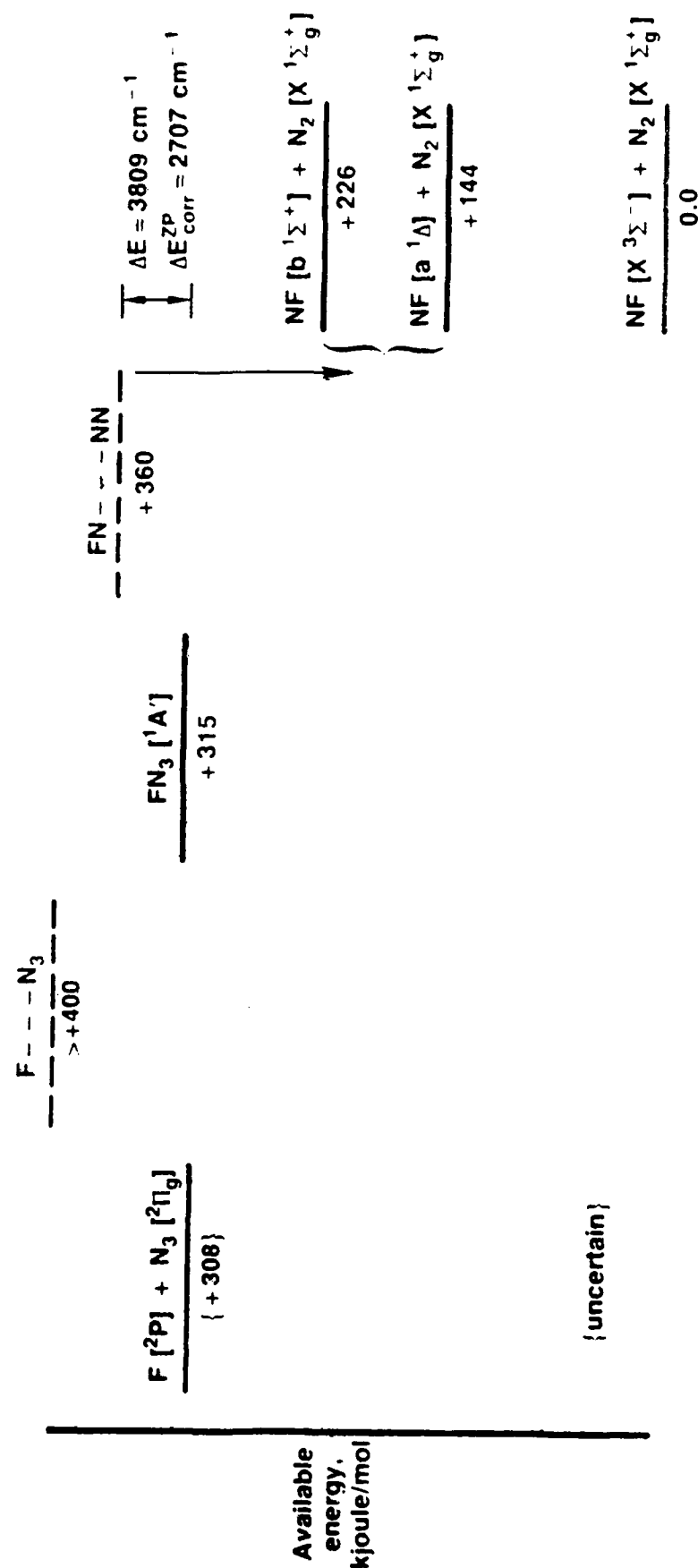
Difluoroaminoborane



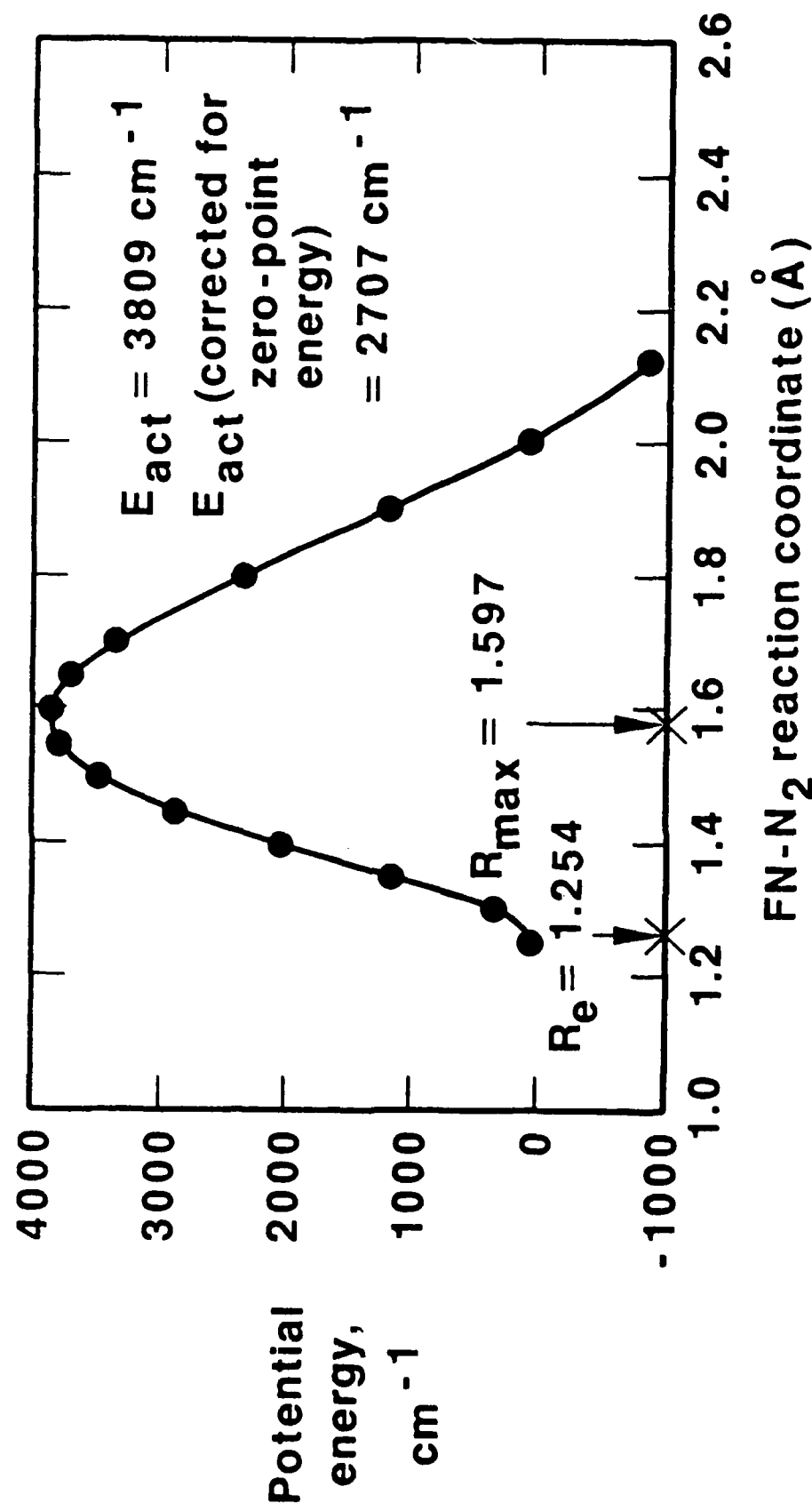
Asymmetric
dinitrogen dioxide



ENERGETICS OF THE CHEMICAL SYNTHESIS OF FLUORINE AZIDE (FN₃)



FN₃ DISSOCIATION PATHWAY



RB1788TX.001

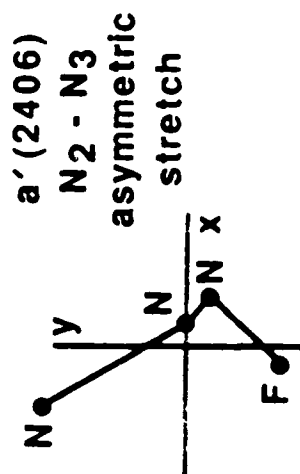
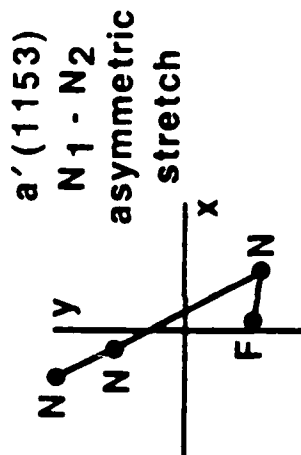
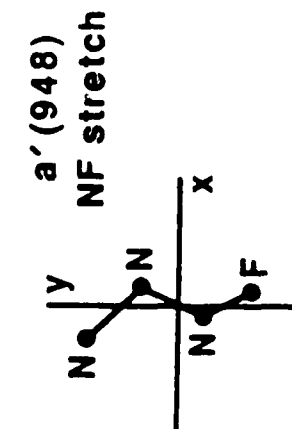
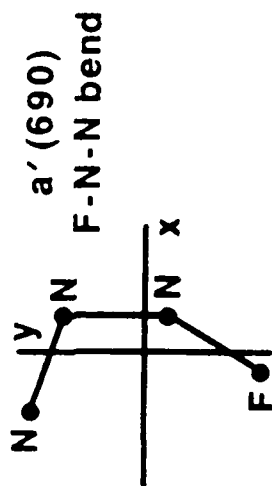
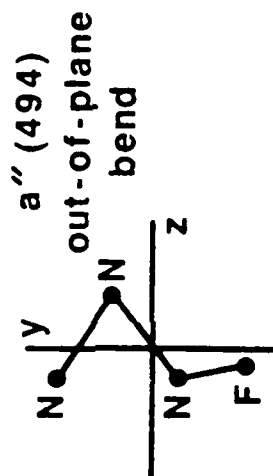
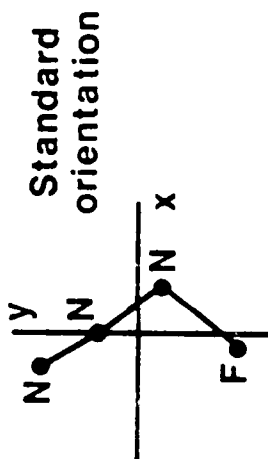
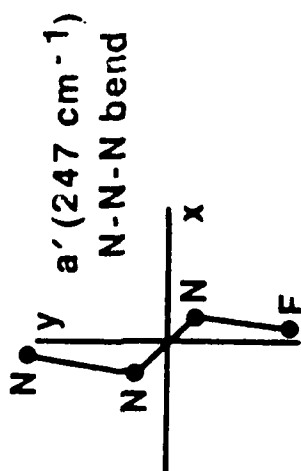
FLUORINE AZIDE (FN₃) FREQUENCY ANALYSIS

Normal mode	Frequency (cm ⁻¹)		
	Calculated		Experiment
	HF	MP2	Milligan & Jacox Gholivand
a' (N-N-N bend)	281	247	- 241
a" (out-of-plane bend)	606	494	503 504
a' (F-N-N bend)	757	690	654 658
a' (N-F stretch)	1045	948	869 874
a' (N ₁ -N ₂ asymmetric stretch)	1225	1153	1086 1090
a' (N ₂ -N ₃ (asymmetric stretch))	2386	2406	2034 2037

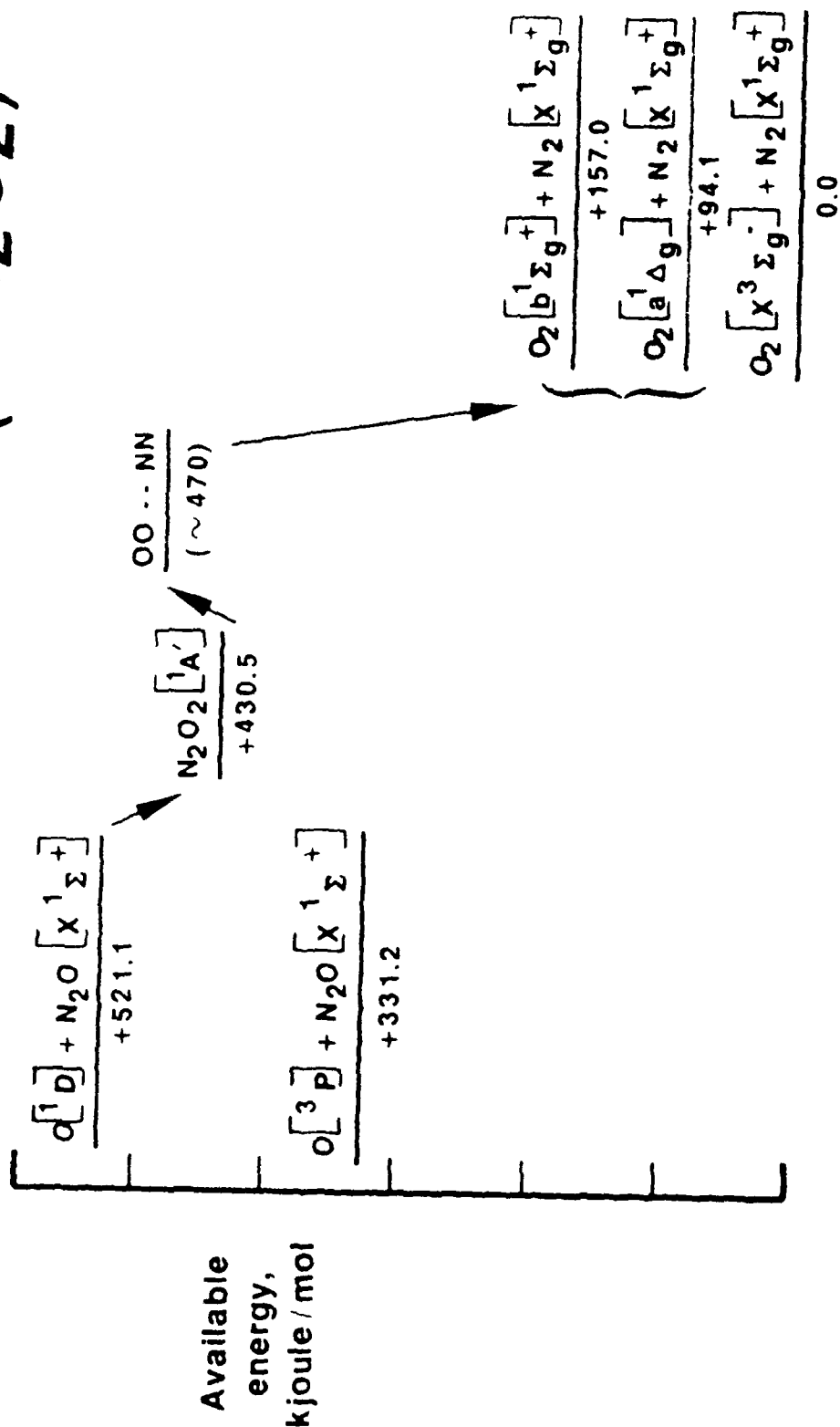
References: D.E. Milligan and M.E. Jacox, J. Chem. Phys. 40, 2461 (1964); K. Gholivand, J. Inorg. Chem., in press

RB1788TX.003

THEORETICAL VIBRATIONAL ANALYSIS OF FLUORINE AZIDE (FN_3)



ENERGETICS OF THE CHEMICAL SYNTHESIS OF ASYMMETRIC DINITROGEN DIOXIDE (α -N₂O₂)



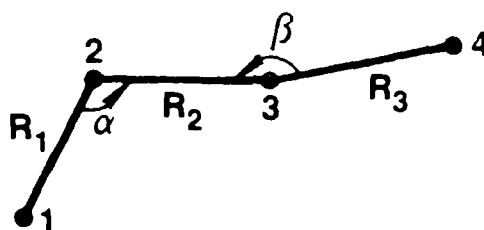
RD1642TK 001

ASYMMETRIC DINITROGEN DIOXIDE (a-N₂O₂) FREQUENCY ANALYSIS

Normal mode	Frequency (cm ⁻¹)	
	HF	MP2
a' (O-O-N bend)	188	210
a'' (Out-of-plane bend)	648	498
a' (O-N-N bend)	291	568
a' (O-O stretch)	697	656
a' (O-N asymmetric stretch)	1262	1200
a' (N-N asymmetric stretch)	2677	2150

RD1642TX.004

OPTIMIZED GEOMETRIES OF AZIDES

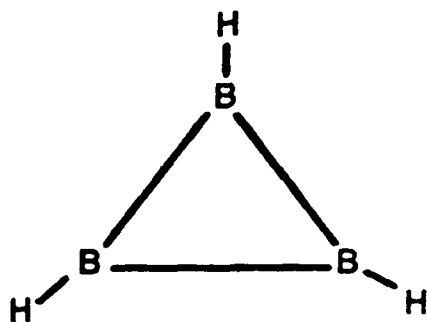


Compound	Theory	R_1 (Å)	R_2 (Å)	R_3 (Å)	α (deg)	β (deg)
HN ₃	SCF	1.0055	1.2381	1.0987	108.181	173.815
	MP2	1.4309	1.2799	1.1521	103.765	171.803
FNCO	SCF	1.3737	1.2387	1.1354	109.846	173.235
	MP2	1.4185	1.2622	1.1765	110.717	168.914
a-N ₂ O ₂	SCF	1.7574	1.2024	1.0844	103.966	179.506
	MP2	1.5305	1.2272	1.1548	103.591	179.488
	CISD	1.5815	1.2238	1.1072	102.840	179.360
FNBF	SCF	1.2993	1.2068	1.2871	180.000	180.000
	MP2	1.3394	1.2491	1.3069	154.650	169.291

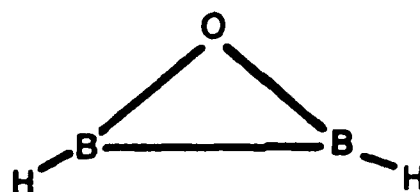
Experimental bond length (Å)

N-N	1.098	H-N	1.041	F-N	1.308	B-N	1.281
C-O	1.128	O-O	1.216	N-O	1.151	B-F	1.262

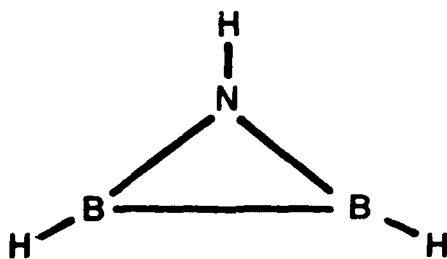
C. HIGH ENERGY BORON STRUCTURES



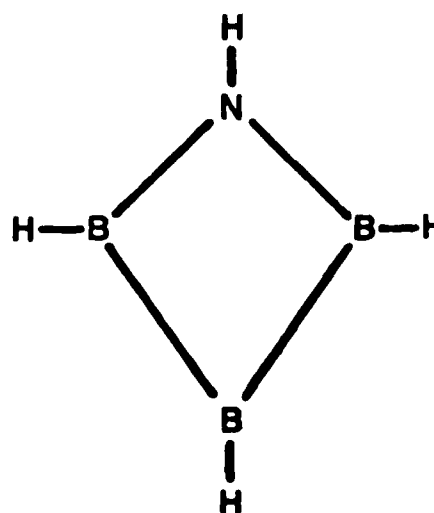
a) B_3H_3 (D_{3h})
cyclotriborane



b) B_2H_2O (C_{2v})
1, 2 epoxydiborane/diborylene oxide
c: ethylene oxide



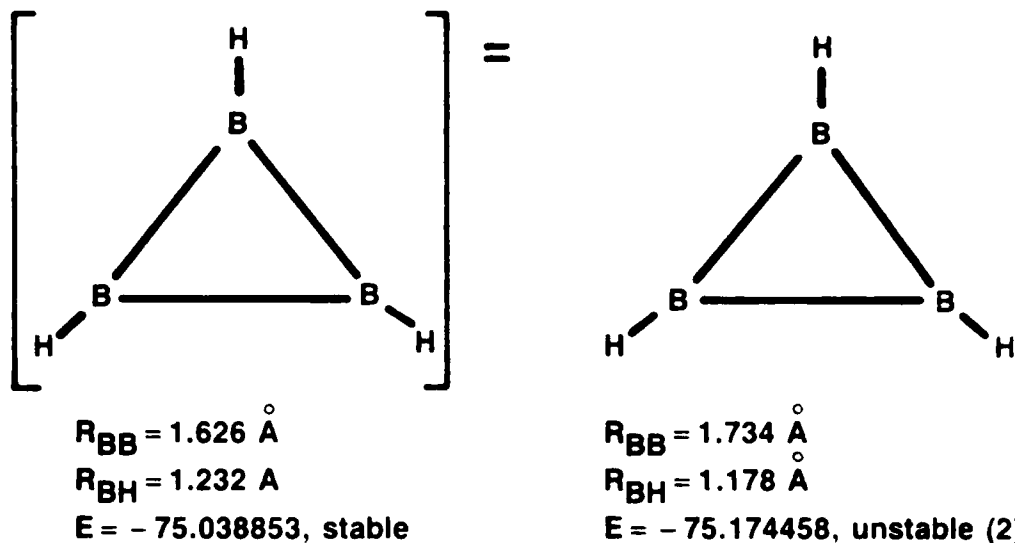
c) B_2H_2NH (C_{2v})
iminodiborane
c: aziridine/ethyleneimine



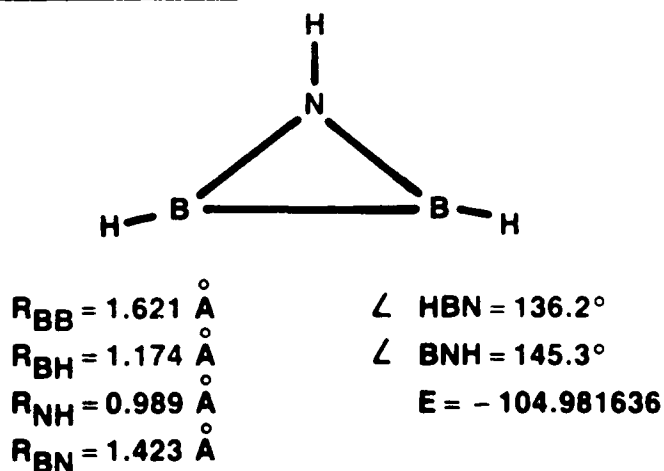
d) B_3H_3NH (C_{2v})
triboryleneimine
c: azetidine/trimethyleneimine

CYCLIC BORON COMPOUNDS

Cyclotriborane (B_3H_3)



Iminodiborane (B_2H_2NH)



<u>Frequencies (cm^{-1})</u>											
B_1	A_1	A_2	B_2	B_2	B_1	A_1	B_2	A_1	B_2	A_1	A_1
700	818	921	923	989	1000	1110	1268	1423	2878	2916	3965

CONCLUSIONS

1. Tetrahydrogen (H_4), LiH_3 and Li_4 are not stable molecules in their ground state in C_{3v} symmetry.
2. Li_3H is stable in its ground state in C_{3v} symmetry. Additional calculations of the energetics of Li_3H are in progress.
3. All of the azide-like structures: FN_3 , $FNCO$, $a-N_2O_2$, and $FNBF$, are vibrationally stable in the lowest $^1A'$ state with predicted high positive heats of formation. FN_3 also has a stable low-lying $^3A''$ state.
4. B_3H_3 has no stability as a D_{3h} structure. The anion, $B_3H_3^-$, is stable as predicted by Lipscomb's rules. B_2H_2NH is stable as a C_{2v} structure with symmetry 1A_1 . Preliminary thermodynamics indicate, however, that B_2H_2NH is not very energetic.
5. Best systems studied to date: $a-N_2O_2$ and $FNBF$
6. Areas for further study: H_n , Li_mH_n structures, azides and further simple boron compounds

**METASTABLE MOLECULAR FUELS:
THEORETICAL STUDY OF ION-PAIR STATES
LOW-LYING SURFACES OF H₃O**

Roberta P. Saxon

Dahbia Talbi

SRI International

RA M 2531 1

OBJECTIVE

Predict new energetic metastable molecular species that do not decay by radiation, tunneling, or other means when isolated in vacuum.

PROPOSAL

Ion-pair bonding between stable negative ions may lead to high-energy (locally) bound states that have not been studied previously.

Example: H_4

METASTABLE MOLECULAR FUELS:
THEORETICAL STUDY OF ION-PAIR STATES - LOW-LYING SURFACES OF H_3O^+

Roberta P. Saxon and Dahbia Talbi
SRI International
Menlo Park, California 94025

Metastable molecular fuels, long-lived molecular species that do not decay by radiation, tunneling, or other means, when isolated in vacuum, have been proposed as the basis for possible new propulsion schemes. The recent prediction of an energetic excimer state of H_4 suggests the possibility of a whole series of molecules bound by the Coulomb attraction between a stable positive ion and a stable negative ion. The fate of an ion-pair species, once formed, will depend sensitively on the details of the potential surfaces that govern decay processes such as optical transitions, predissociation, and internal conversion. This theoretical program is devoted to examining ion-pair species composed of first-row atoms that could serve as candidate fuels. In this paper, CASSCF-FOCI calculations on the low-lying doublet and quartet potential surfaces of the H_3O system are reported.

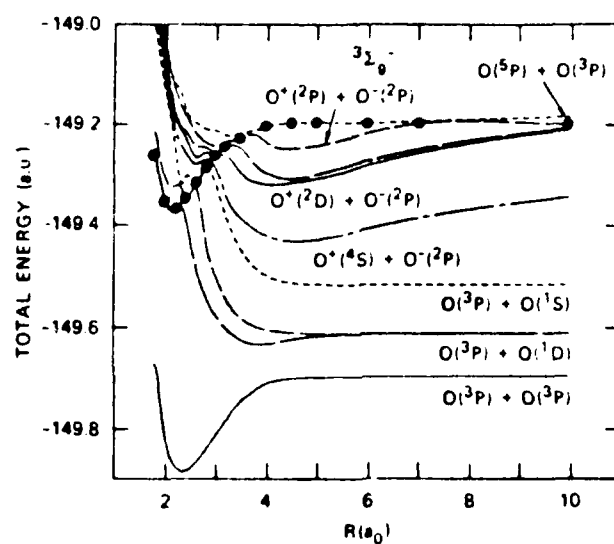
Consistent with our model of an ion-pair state as an H_3^+ equilateral triangle with an O^- located above the center of the triangle, our calculations to date have concentrated on C_{3v} geometries. A DZP basis set augmented by diffuse s and p functions on O was used. The correlation diagram linking the H_3O states studied here to states of the separated fragments has been established. The connection between this work and the portions of the ground state (doublet) potential surface considered by previous workers^{1,2} i.e. the H_3O local minimum and the $\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$ transition state has also been explored. While portions of the lowest potential surface corresponding to the ion-pair H_3^+-O^- can be identified, at the minimum energy, the lowest state may be described as H_3O^+ with an electron in an oxygen Rydberg orbital, in agreement with the previous report². This conformation is known to dissociate to $\text{H}_2\text{O} + \text{H}$. There is no barrier inhibiting conversion of the ion-pair geometry to the Rydberg geometry. Within the restricted C_{3v} geometry, however, a stable ion-pair state with H-H distance very similar to that in the H_3^+ ion is observed on the first excited doublet potential surface. Investigation of this surface in unrestricted geometries is underway.

[†]Work supported by Air Force Flight Test Center under contract F04611-86-C-0070

¹S. P. Walch and T. H. Dunning, *J. Chem. Phys.* **72**, 1103 (1980).

²K. S. E. Niblaeus, B. O. Roos, and P. E. M. Siegbahn, *Chem. Phys.* **25**, 207 (1977).

ION-PAIR STATES IN O₂



R.P.Saxon and B. Liu
J. Chem. Phys. 73 (876) 1980

RA-m-2531-15

SELECTION OF SPECIES

Maximum specific impulse

$$I_{sp} \propto \sqrt{\frac{\text{heat of reaction}}{\text{mass of products}}}$$

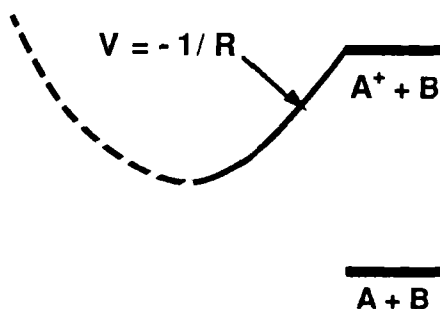
- low molecular weight

H_3^+ positive ion - 1st row negative ion

- optimal electron affinity - a tradeoff

large EA \Rightarrow stable negative ion

small EA \Rightarrow high-energy minimum



ELECTRON AFFINITIES

<u>Neutral</u>	<u>EA (eV)</u>
H	0.75
O	1.46
F	3.40
O ₂	0.43
O ₃	2.10
Li	0.62

RA-M-2531-4

CALCULATIONS ON H_3O

BASIS SETS:

4-31G (preliminary survey)
DZP + diffuse s and p on O

CASSCF (Complete Active Space)

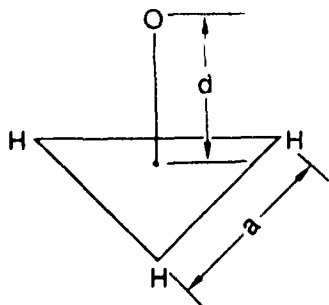
9 active electrons (include O (2s))
250 configurations C_s symmetry
converge on 1 $^2A'$ state
solution totally symmetric

FOCI (First Order CI)

Single excitations with respect to CAS
DZP: 14902 configurations $^2A'$

SOCI (Second Order CI)

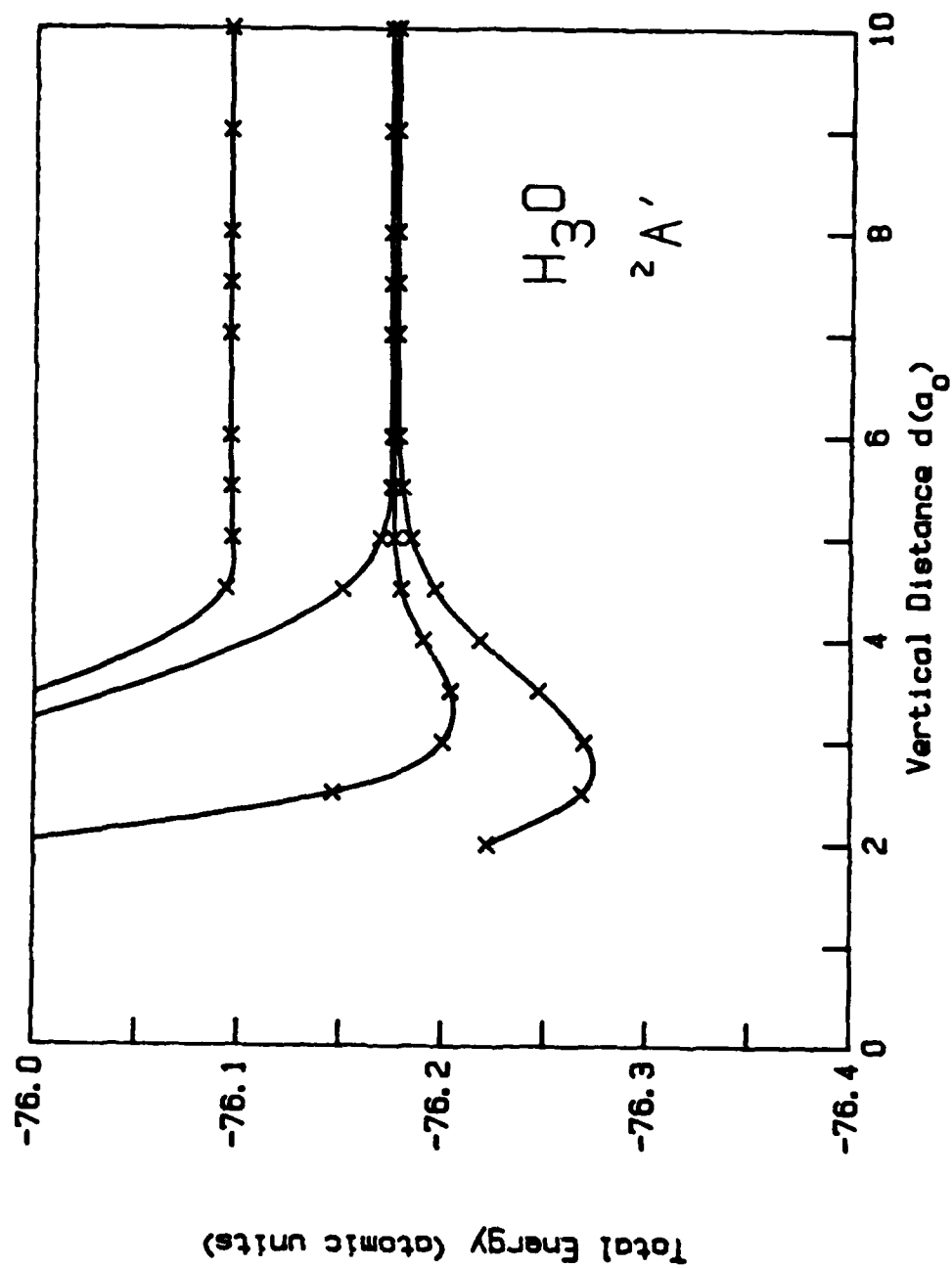
DZP: 370330 configurations



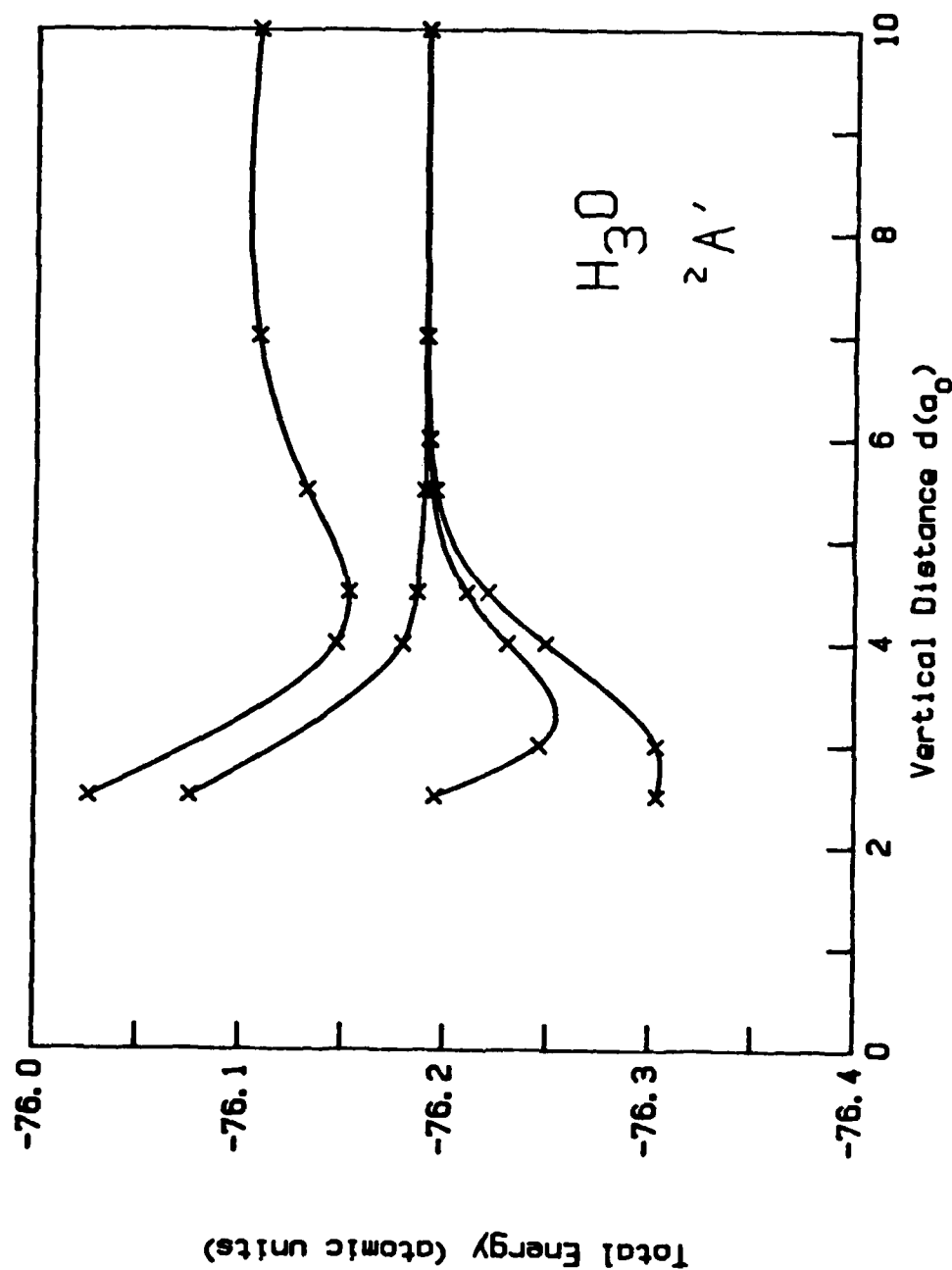
Calculations to date:

molecule in C_{3v} symmetry
calculations in C_s symmetry

RA-m-2531-5



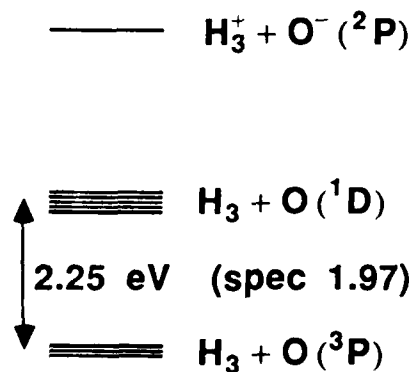
H_3O 4-31G MCSCF Results at Fixed H-H Distance = $1.65a_0$



H_3O^+ 4-31G FOCI Results at Fixed H-H Distance = $1.65a_0$

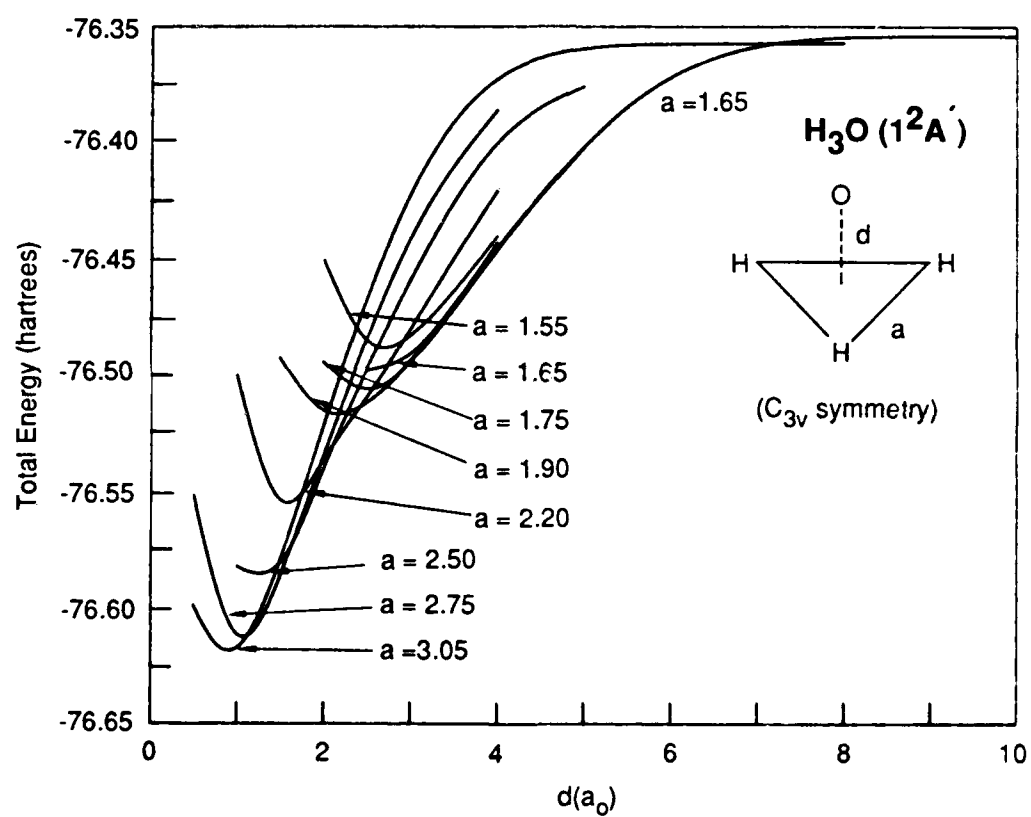
INDICATIONS FROM PRELIMINARY 4-31G RESULTS

- 1) Can locate attractive region of potential surface due to ion-pair bonding
- 2) Asymptotes can be interpreted
(FOCI - $a = 1.65 a_0$, $d = 10.0 a_0$)



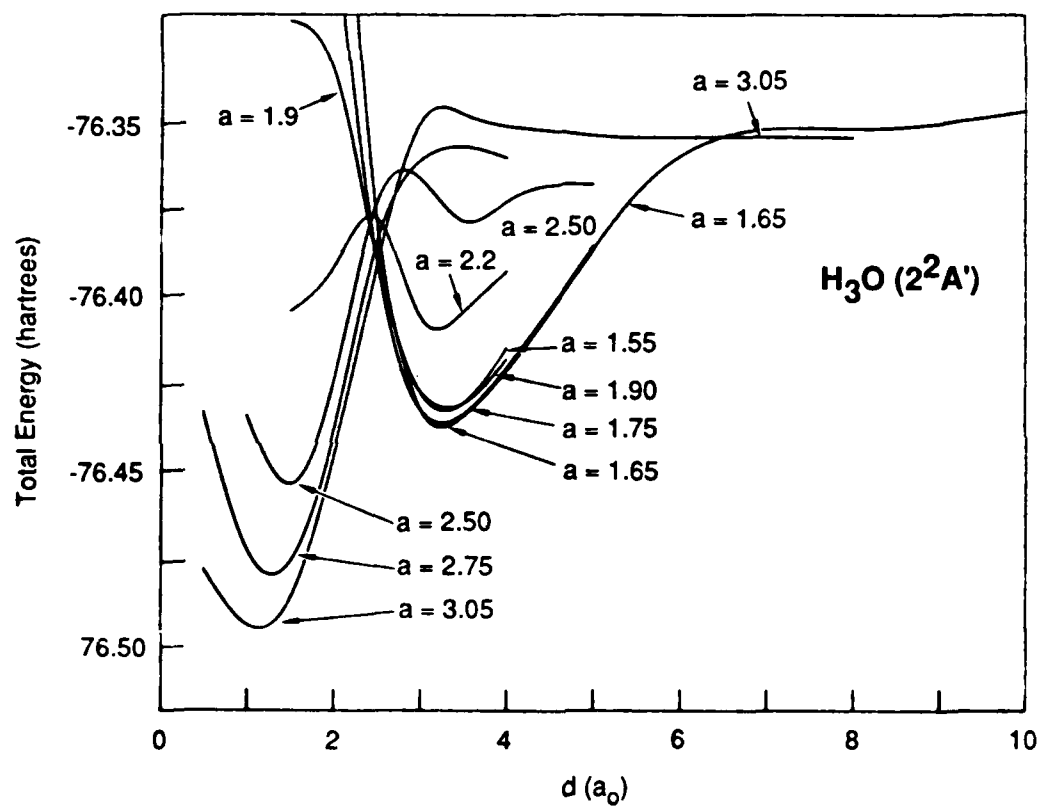
RA-M-2531-6

**DZP/FOCI RESULTS AT FIXED H-H DISTANCE
AS A FUNCTION OF VERTICAL DISTANCE**



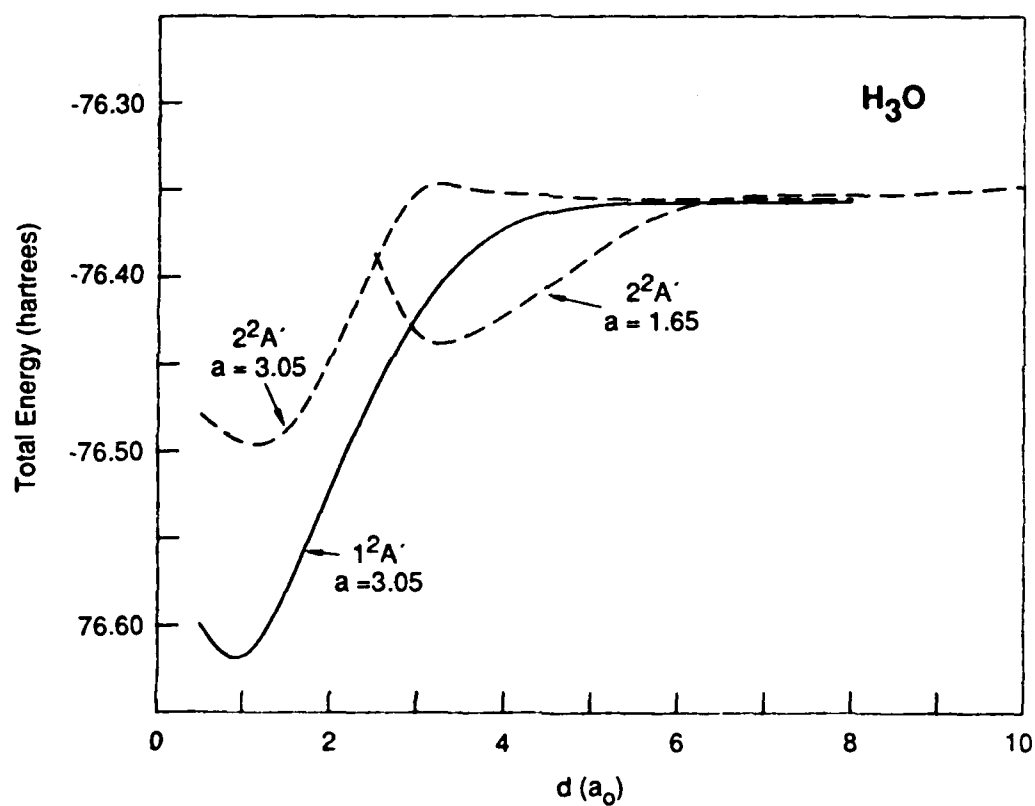
RA-m-2531-8

**DZP/FOCI RESULTS AT FIXED H-H DISTANCE
AS FUNCTION OF VERTICAL DISTANCE**



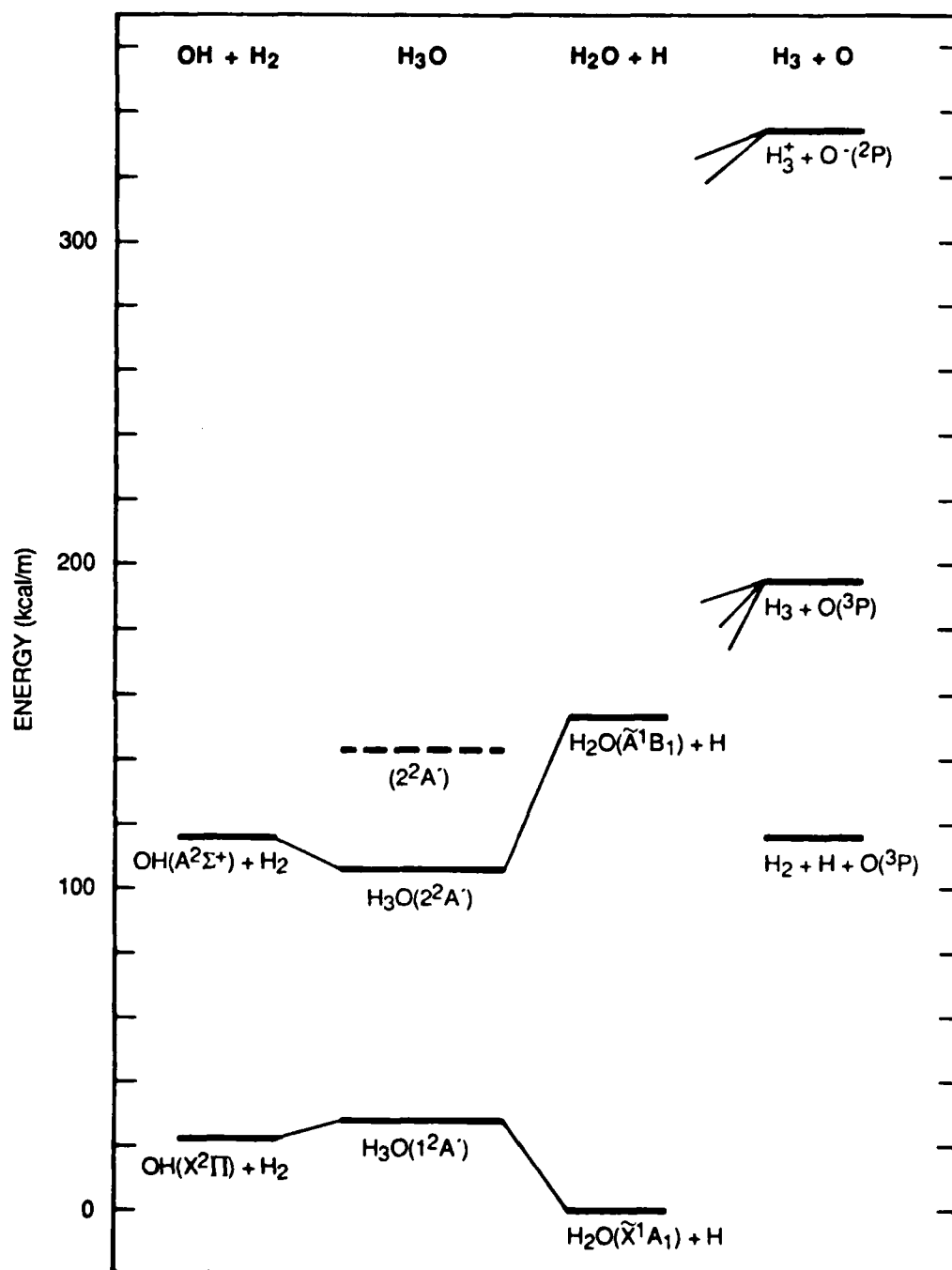
RA-m-2531-9

**DZP/FOCI RESULTS AT FIXED H-H DISTANCE
AS FUNCTION OF VERTICAL DISTANCE**



RA-m-2531-10

H₃O CORRELATION DIAGRAM (2A' Symmetry)



RA-2531-7

Notes on Correlation Diagram

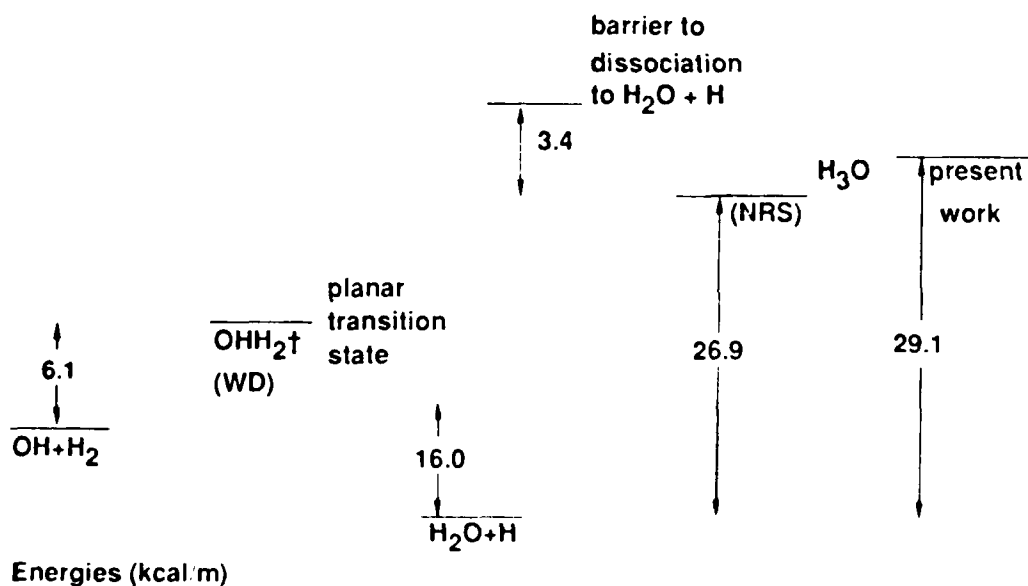
1. H_3O , H_3 , and H_3^+ calculated at C_{3v} geometries
2. Energies determined at equilibrium geometries
3. Ground state surface of H_3 is repulsive; energy independent of H-H distance, a , for $a > 1.65a_0$
4. Energies from DZP/FOCI calculations except:
 - a. $\text{OH}(\text{A}^2\Sigma^+)$ and $\text{H}_2\text{O}(\bar{\text{A}}^1\text{B}_1)$ spectroscopic excitation energy
 - b. H_2 experimental binding energy used to place $\text{H}_2 + \text{H} + \text{O}$ with respect to $\text{H}_3 + \text{O}$

H₃O LOWEST POTENTIAL SURFACE RELATIONSHIP TO OTHER STUDIES

(WD) S. P. Walch and T. H. Dunning
J. Chem. Phys. 72, 1303 (1980)
POL-CI

E. Kraka and T. H. Dunning, *unpublished*

(NRS) K. S. E. Niblaeus, B. O. Roos, and P. E. M. Siegbahn
Chem. Phys. 25, 207 (1977)
UHF-SDCI



GEOMETRY DETERMINATION

UHF

FOCI

$$a = 3.05a_0$$

$$\text{at } a = 3.05a_0$$

$$d = 0.62a_0$$

$$d = 0.92a_0$$

H₃O wave function qualitatively same

H₃O⁺ + diffuse s on O

RA m 2531-12

H₃O CONCLUSIONS TO DATE

C_{3v} Restricted Geometries

DZP/FOCI

1²A'

Large portions of potential surface may be characterized as ion-pair

Lowest energy (in C_{3v} geometry) corresponds to 0(3s) Rydberg and dissociates to H₂O + H with small barrier

2²A'

Ion-pair minimum (in C_{3v} geometry) at $\sim a = 3.05 a_0$, $d = 1.0 a_0$ 106.5 kcal/m above H₂O + H

No adiabatic correlation with ground state OH + H₂ or H₂O + H

Bound with respect to OH(A² Σ^+) + H₂ and H₂O(A¹B₁) + H

Second ion-pair local minimum at $a = 1.65 a_0$, $d = 3.5 a_0$ 143.9 kcal/m above H₂O + H

Higher in energy than OH(A² Σ^+) + H₂

Barrier to 2²A' lower minimum

H₃O WORK IN PROGRESS

2A'

SOCI for better determination of absolute energies

2A''

Characterization of surfaces

**At most C_{3v} geometries, 1²A''
equivalent to 2²A'**

1²A'' correlates to ground state OH + H₂,

QUARTETS

Characterization of surfaces

**Much higher in energy - small binding, if
any, with respect to H₃ + O (³P)**

**No correlations with lowest OH + H₂O + H
asymptotes**

RA-M-2531-14

ARIES Contractor's Meeting
Rosalyn, VA, 12-13 May 1987

High Spin States of CO and CH
by
Daniel D. Konowalow and Marcy E. Rosenkrantz
State University of New York at Binghamton
Binghamton, N.Y. 13901

Ab Initio Calculations On High Spin States of CO and CH

by

DANIEL D. KONOWALOW
Department of Chemistry
SUNY-Binghamton, Binghamton, NY 13901

ABSTRACT

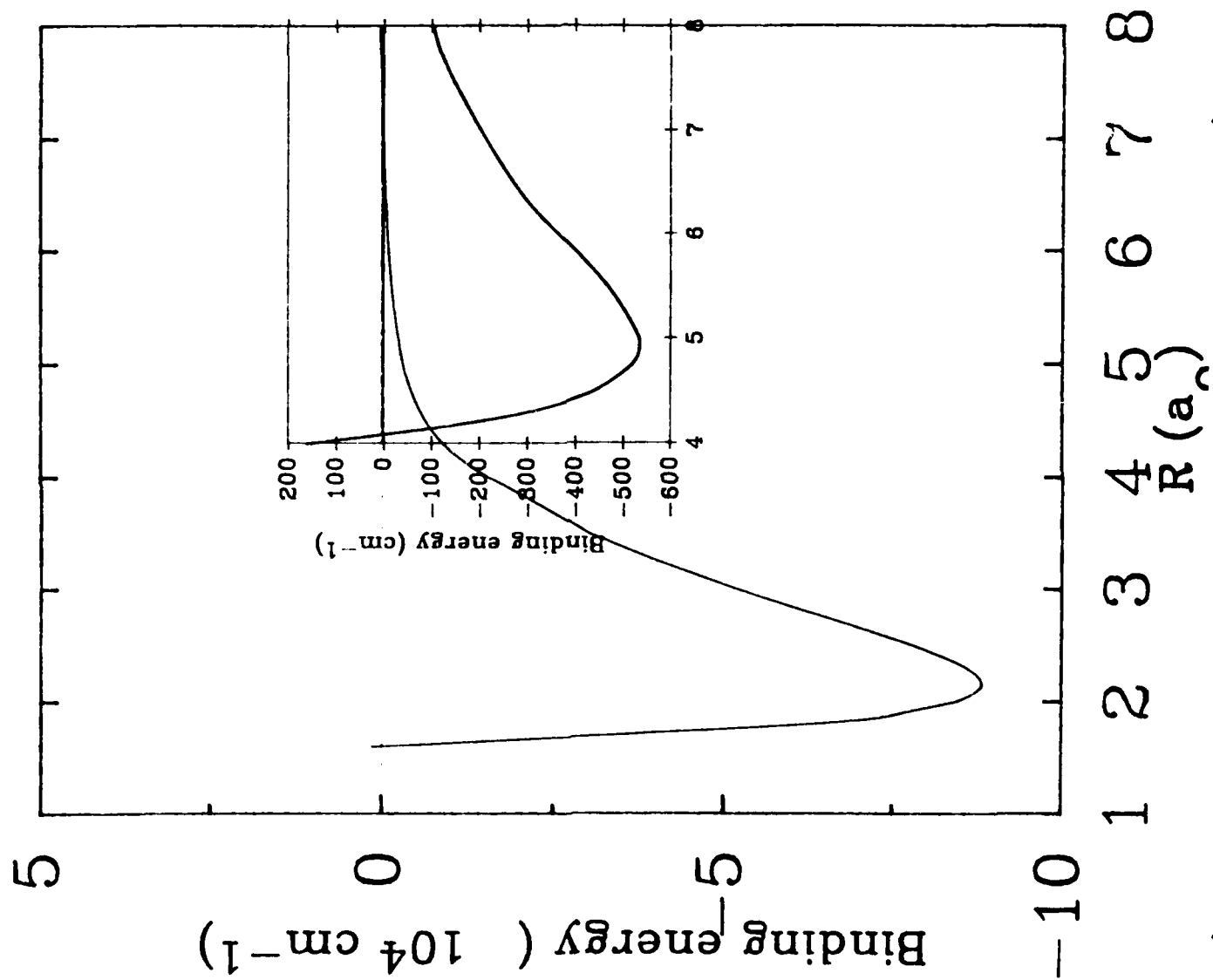
As part of our current interest in potential novel energy storage devices we have investigated several high spin states of CO and CH. The results of our calculations on the $^5\Sigma^+$ and $^5\Pi$ states of CO and the $^4\Sigma^-$ state of CH will be discussed. The possibilities for spin-orbit interactions involving these high-spin states will also be considered.

The basic idea behind this phase of our research is to investigate the properties of pairs or aggregates of high spin atoms which may combine to form a deeply bound low spin molecule. The binding energy of the ground state molecule may in principle be stored as suitably protected atoms or else as high-spin van der Waals molecules. Examples of the latter are the $^3\Sigma_u^+$ state of H_2 which could release about 4.5 eV on a spin flip and formation of the $^1\Sigma_g^+$ state or the $^7\Sigma_u^+$ state of N_2 which could undergo a series of spin flips to form the ground $^1\Sigma_g^+$ state with the release of about 9.7 eV. Figure 1 compares our $^1^5\Sigma^+$ van der Waals curve of CO together with the ground $^1\Sigma_g^+$ state potential curve to emphasize the tremendous energy storage potential of such a high-spin van der Waals molecule.

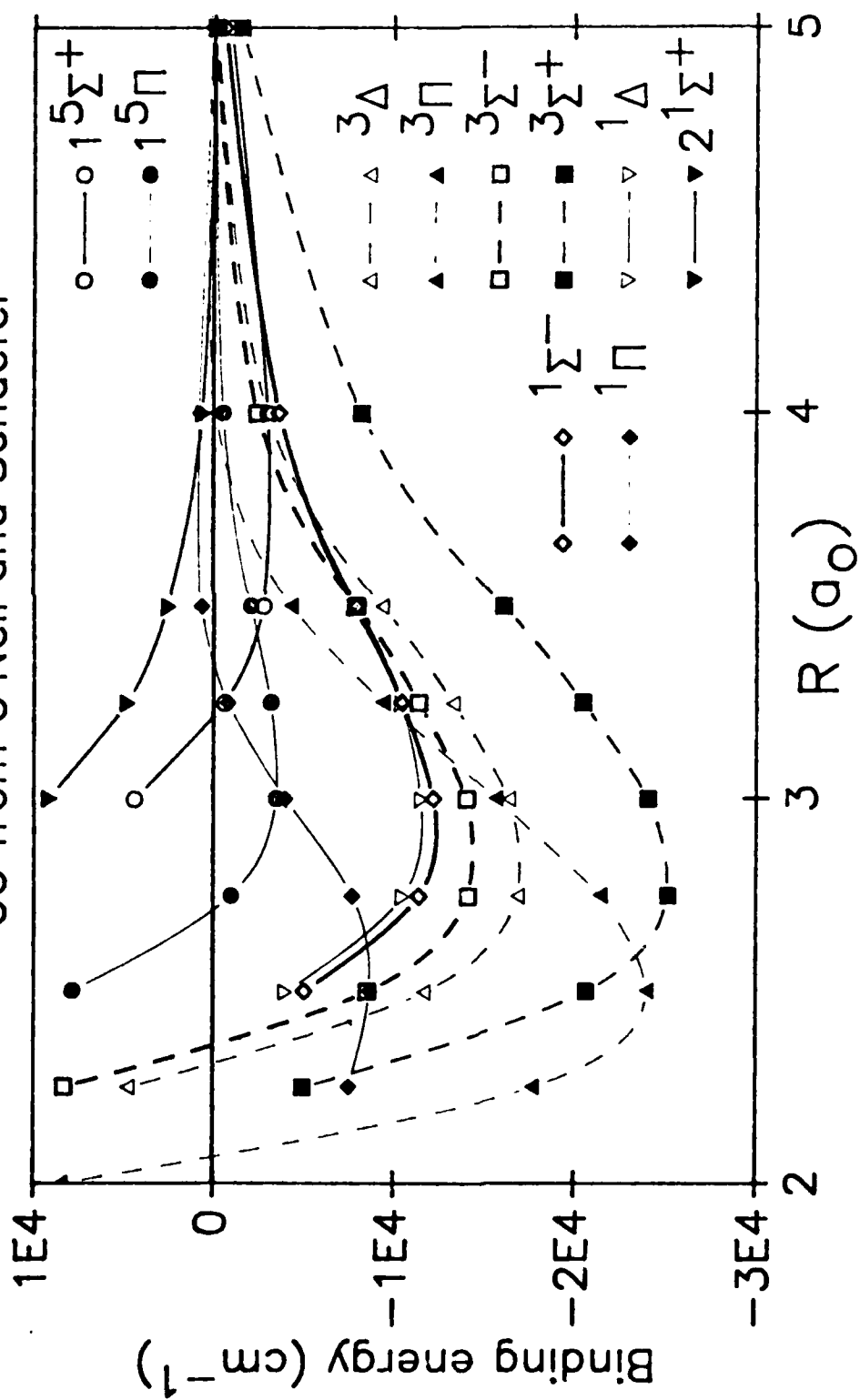
The $^7\Sigma_u^+$ state of N_2 has been examined from this point of view by Ferrante and Stwalley [J. Chem. Phys. 78, 3107 (1983)] who estimated its potential curve by adding an estimate of the dispersion attractive energy to their calculated repulsive self consistent field (SCF) energy. Their SCF plus dispersion potential had a D_e of just over 40 cm^{-1} . Later, Partridge, Langhoff, and Bauschlicher [J. Chem. Phys. 84, 6901 (1986)] found from an exhaustive set of configuration interaction (CI) computations in terms of a substantial basis set and careful estimates of basis set superposition errors that the D_e value was in fact only about 21 cm^{-1} .

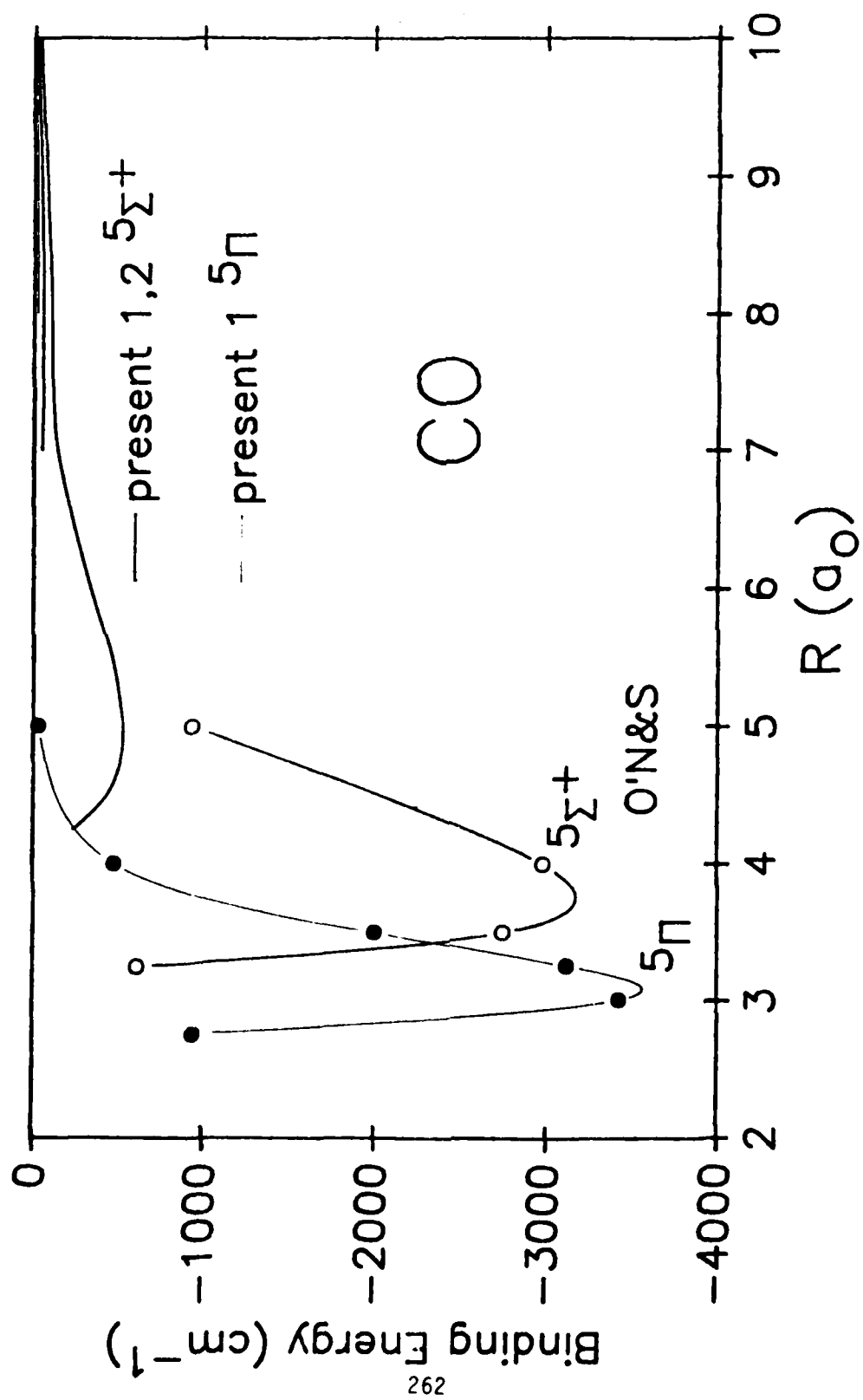
In view of these new results Ferrante and Stwalley [J. Chem. Phys. 85, 1201 (1986)] showed that their earlier values of critical temperature and triple point temperature, for example, had to be revised downward by about a factor of two. The point of this recitation is to note that extreme care must be taken to assure the highest possible accuracy in the calculation of such weakly bound van der Waals potential curves if they are to provide useful estimates of thermal properties, for example.

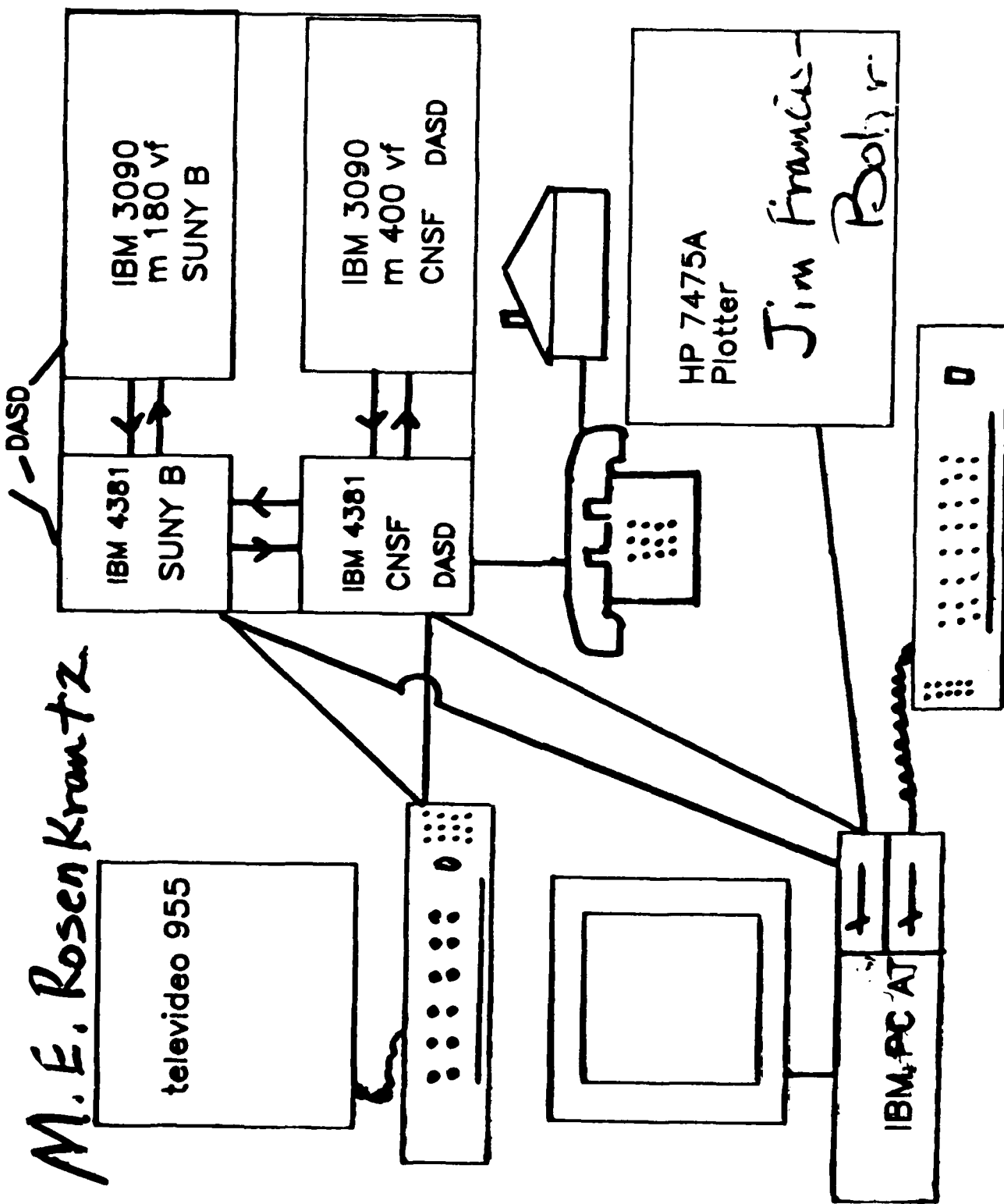
We are currently investigating high spin states of CO which promise to give greater specific impulse than high spin N_2 . The bulk of the experimental and theoretical information available on CO treats mainly spin singlets and to a much lesser extent spin triplets. The only published information on quintets we found is the pioneering work of O'Neill and Schaefer (ONS) [J.



CO from O'Neil and Schaefer







Polarizabilities

α_d	m_l	C	O	N
	0	10.10 (10.10)	5.005 (5.14)	7.353 (7.36)
	1	12.99 (13.05)	4.54 (4.58)	25.673 (25.66)
α_q	0	41.60 (41.73)	20.32 (20.61)	
	1	61.80 (61.28)	14.74 (15.05)	
α_o	0	449.6	141.5	
	1	697.7	98.4	

Chem. Phys. 53, 3994 (1970)]. Figure 2 displays all their calculated bound states corresponding to the $C(^3P) + O(^3P)$ interaction except for the ground state. Their minimal basis set, full valence configuration interaction calculation is subject to very substantial basis set superposition error (we estimate an error of about 2500 cm^{-1} at $R=4\text{ a}_0$ for the $1\ ^5\Sigma^+$ state) and, thus, can provide only a qualitative guide to our own work. We show in Fig. 3 that the ONS curves for the lowest $^5\Sigma^+$ and $^5\Pi$ states are substantially deeper than our own (primarily due to their BSSE).

Let us describe our own calculations. It is performed with the apparatus shown schematically in Fig. 4, which ably is operated by Marcy Rosenkrantz and Jim Francis-Bohr, among others. We augmented the basis set of Liu and McLean [unpublished] with two s-, two p-, and one each of d-, f- and g- functions needed to optimize the dipole, quadrupole and octupole polarizabilities of the ground state atoms C and O. Our polarizability results are given in Fig. 5 and are compared with available literature values (in parentheses) [H.J. Werner and W. Meyer Phys. Rev. A13, 13 (1976); E.A. Reinsch and W. Meyer Phys. Rev. A18, 1973 (1978)]. The atomic polarization basis is needed in order to insure an adequate description of the long-range interaction energies commonly approximated by the familiar multipole series:

$$E_{\text{Disp}} = -C_6R^{-6} - C_8R^{-8} - C_{10}R^{-10} - \dots$$

Note that we do not use perturbation theory to calculate the long-range interactions, we merely use its familiar language in this discussion.

We have found that there is a substantial amount of configuration mixing between the two lowest $^5\Sigma^+$ states of CO, especially in the region of $5-8\text{ a}_0$. Unless we were extremely careful with our choice of reference state(s) and input vectors on which to base the multireference second order CI (SOC1) calculation, we obtained potential curves that appeared to be nonsense. We shall not regale you with the details of our early computations, but rather describe the approach we have taken to obtain our current best results.

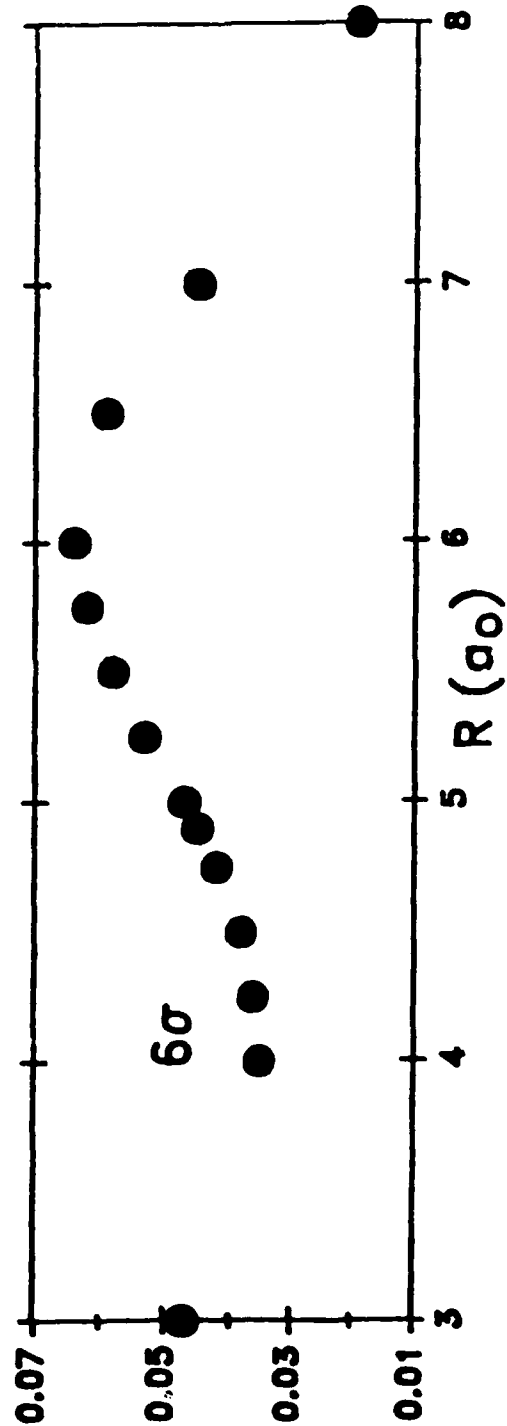
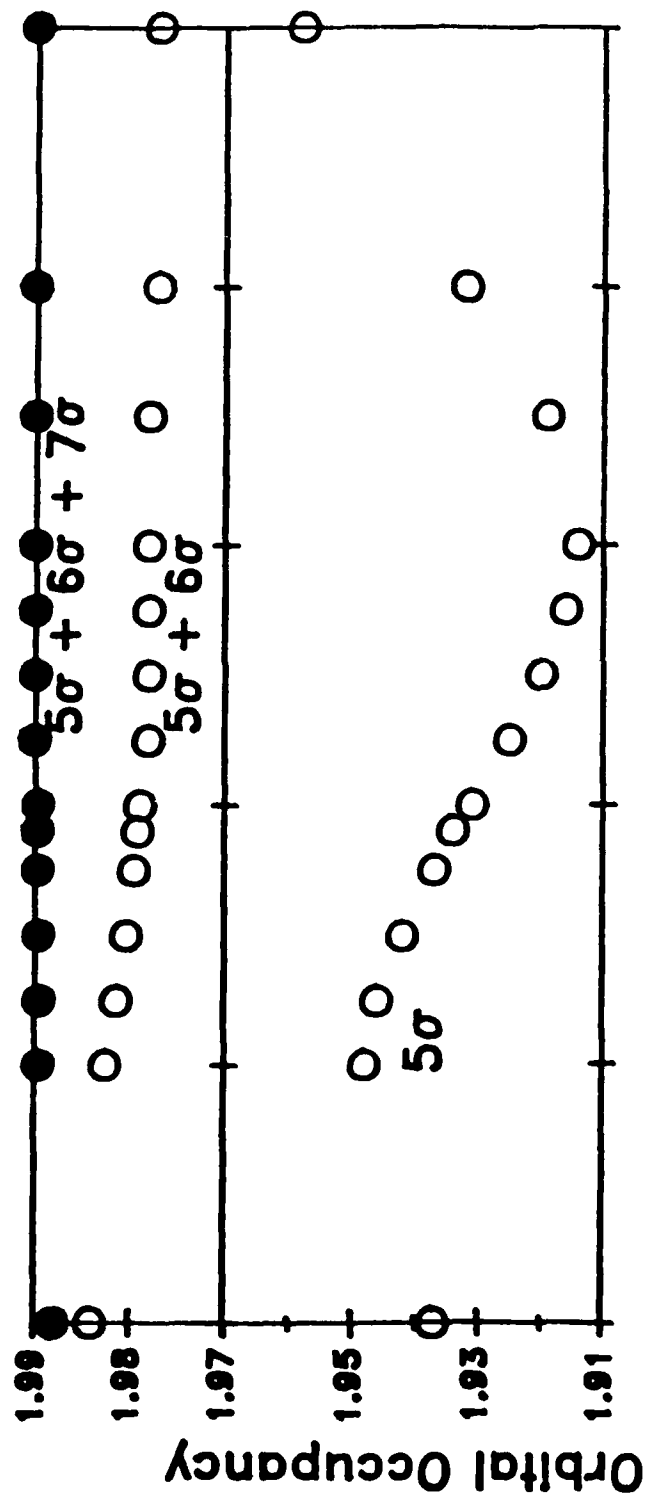
First we performed SOC1 calculations on the $1,2\ ^5\Sigma^+$ states where the excitations were performed from the seven configurations that arise from allowing the six p electrons to occupy any of two σ and two π orbitals consistent with $^5\Sigma^+$ symmetry. These calculations employed the molecular

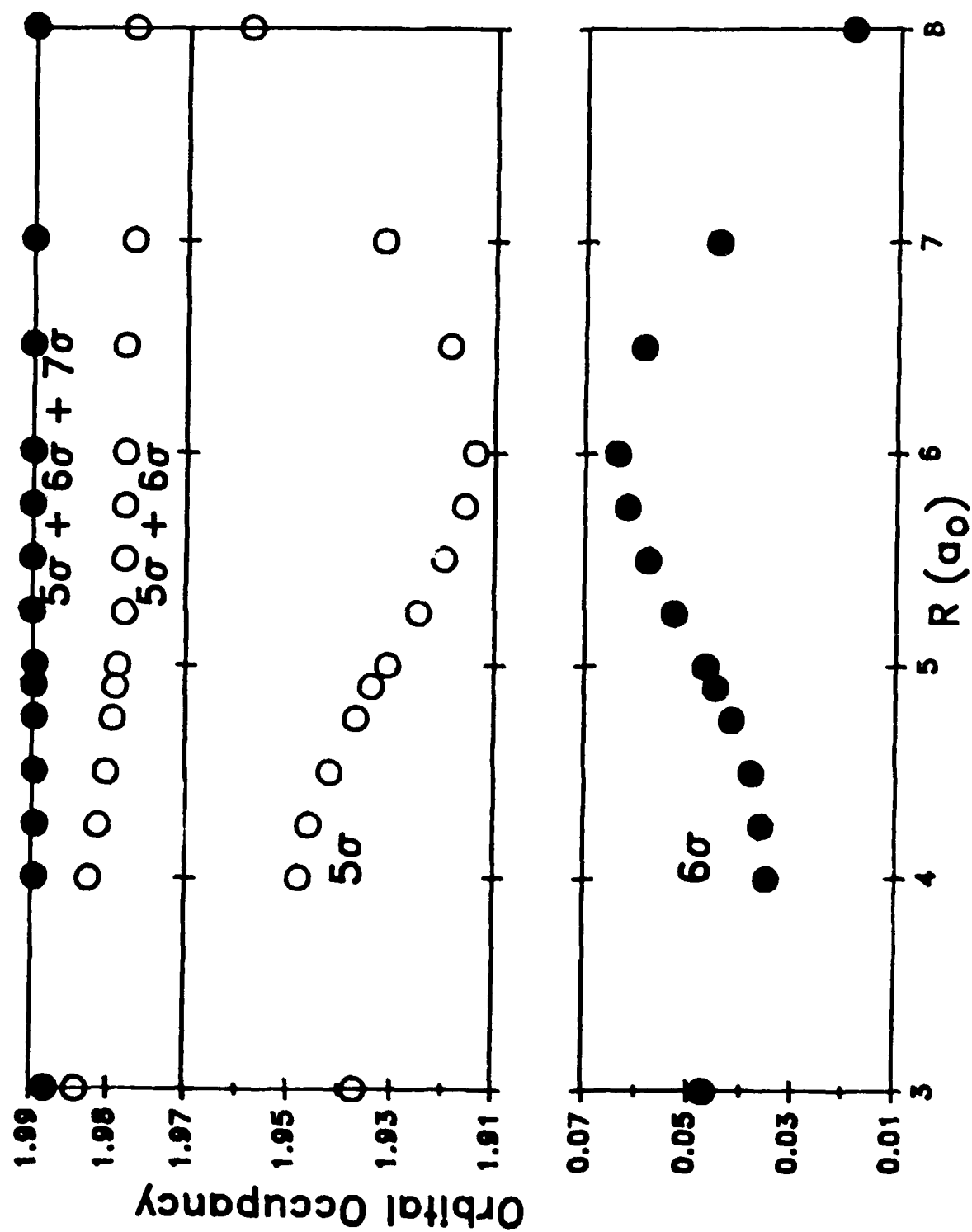
orbitals obtained from an SCF computation on the ${}^5\Sigma^+$ state with the configuration $[]5\sigma 6\sigma 1\pi^3 2\pi$ we then analyzed the natural orbitals as shown in Figs 6 and 7 which suggested that a good multireference SOCI base would obtain from a CASMCSCF in which the six "p" electrons were allowed to occupy any of the three σ and two π orbitals consistent with ${}^5\Sigma^+$ symmetry. The corresponding SOCI comprised about 119,000 configuration state functions (CSF).

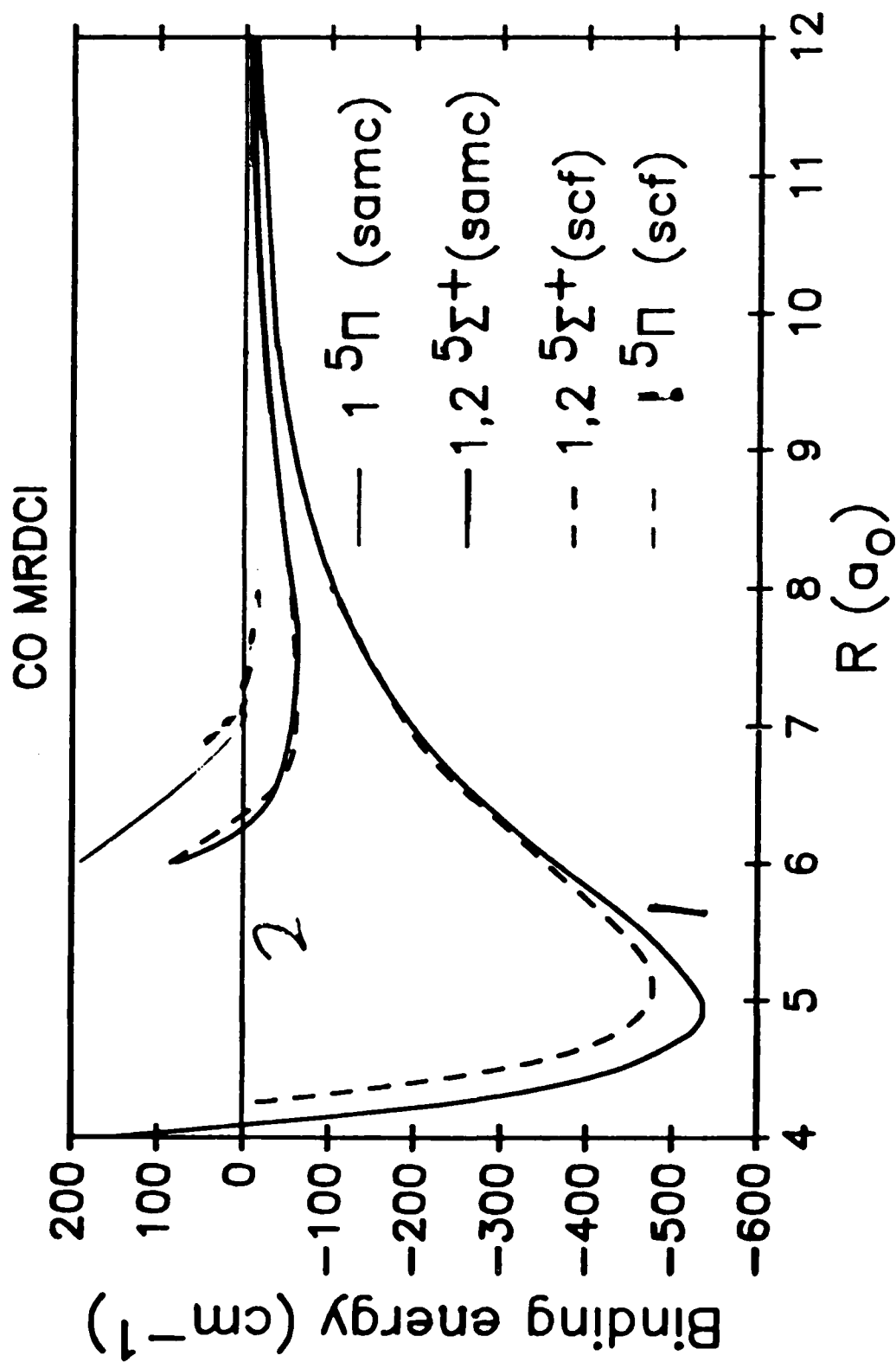
The resulting binding energies for the $1,2 {}^5\Sigma^+$ and ${}^5\Pi$ states are shown in Fig. 8. As shown in Fig. 8, we obtain slightly different results depending on whether our input vectors for the multireference (119,000 CSF) $6/3 + 2$ computation came from the SCF computation for ${}^5\Sigma^+ []5\sigma 6\sigma 1\pi^3 2\pi$ or from a state averaged (1 and 2 ${}^5\Sigma^+$) $6/3\sigma + 2\pi$ MCSCF calculation. We presume that the latter computation is the more reliable.

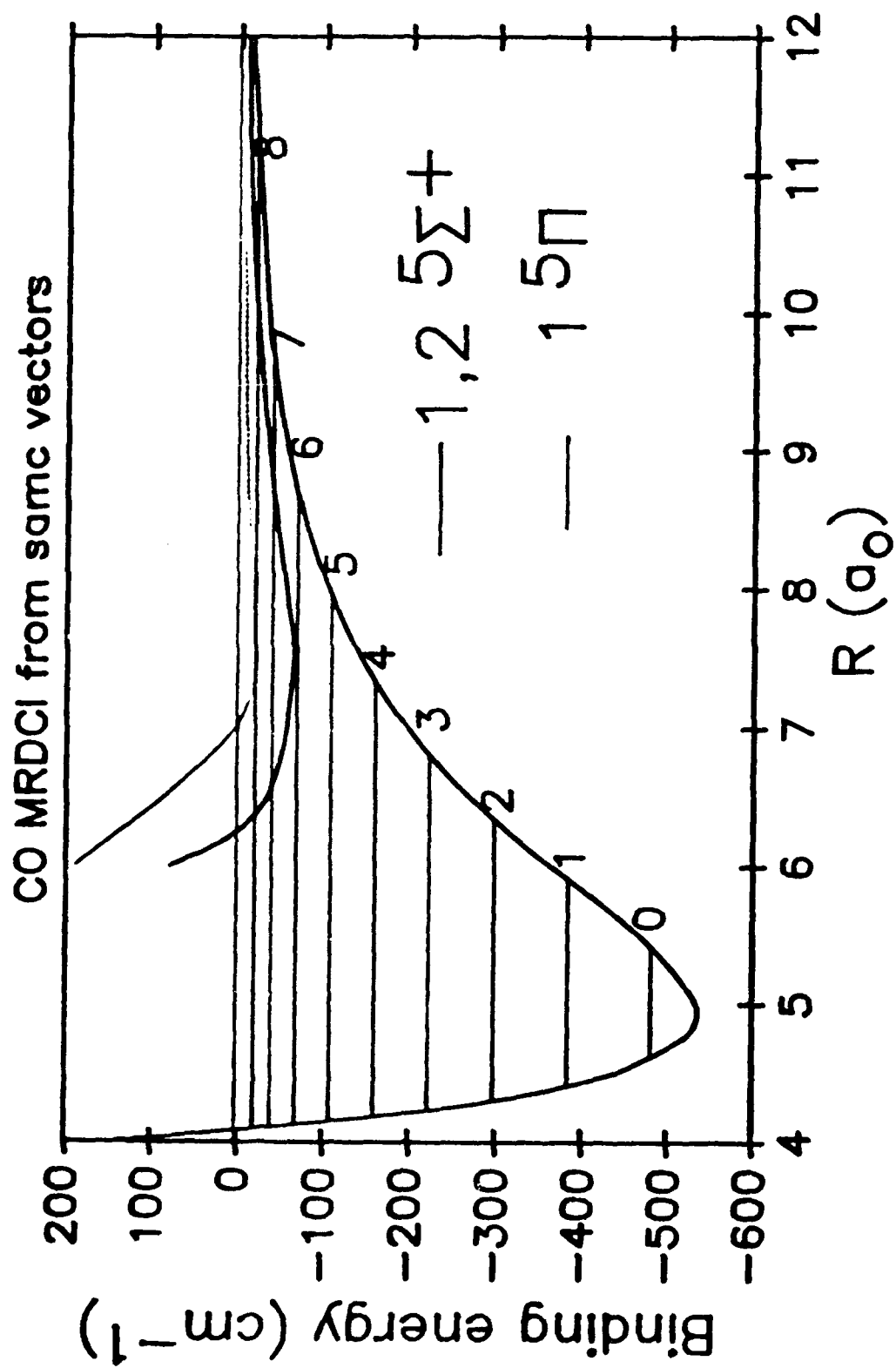
Figure 9 shows that the $1 {}^5\Sigma^+$ state has nine or more bound, $J=0$ vibrational levels and that it is expected to be relatively stable thermally at or below room temperature. Even the $2 {}^5\Sigma^+$ and $1 {}^5\Pi$ states are seen to be at least weakly bound (the former has at least two bound vibrational levels), so they too could be potential energy storage states at sufficiently low temperatures. However, it remains to be seen what the radiative lifetimes of these states are.

We have started on calculations of other high spin quintet and triplet states of CO which correspond to the $C({}^3P) + O({}^3P)$ asymptote. When those calculations are complete we shall be able to consider various decay mechanisms of the potential energy storage states.









Theoretical Studies of Spin-Forbidden Radiative
Processes and Electronically Nonadiabatic Processes
Using ab initio Electronic Structure Methods

James O. Jensen and Byron H. Lengsfeld
Ballistic Research Laboratory
Aberdeen, MD

and

David R. Yarkony
Department of Chemistry
The Johns Hopkins University
Baltimore, MD 21218

Applications of a recently developed methodology¹ for treating spin-forbidden radiative processes within the Breit-Pauli approximation will be reported. Briefly the electronic wavefunctions (Ψ_I) are determined through first order in perturbation theory, $\Psi_I = \Psi_I^O + \Psi_I^I$, with Ψ_I^O and Ψ_I^I expanded in a configuration state function (CSF) basis

$$\Psi_I^O = \sum_k C_k^I \psi_k \quad , \quad 1a$$

and

$$\Psi_I^I = \sum_k V_k^I \psi_k \quad . \quad 1b$$

C^I satisfies the secular equation

$$(H^O - E_I^O) C^I = 0 \quad 2$$

while V^I satisfies

$$(H^O - E_I^O) V^I = -H^{SO} C^I \quad 3$$

where H^{SO} is the full microscopic spin-orbit hamiltonian. The CSF basis, ψ , is developed from orthonormal molecular orbitals determined within the state average MCSCF approximation.

The determination of ψ_1^1 using 1b and 3 is preferred computationally over the traditional eigenfunction expansion method which gives ψ_1^1 as

$$\psi_1^1 = \sum_K \frac{\sum_I \tilde{C}_I^{K\dagger} H_{II}^{SO} \tilde{C}_I^1}{(E_I^0 - E_K^0)} \tilde{C}_K^1 \quad . \quad 4$$

In particular use of eq. 3 permits treatment of spin-forbidden radiative processes originating in coupling to bound states in the continuum ('resonances'). The use of eq. 4 in this instance would be difficult if not impossible.

The situation is illustrated with the determination of the radiative lifetime for the $a^1\Lambda \rightarrow X^3\Sigma^-$ transition in CH^- . Okamura et al.² have reported the lifetime for this transition as $5.9 \pm 0.8, -0.6$ ns. This transition acquires oscillator strength by coupling of the $^1\Lambda$ and $^3\Sigma^-$ states respectively to $^3\Pi$ and $^1\Pi$ states embedded in the $CH + e^-$ continuum. The solution of eq. 3 will be obtained in a large CSF basis ($\sim 10^5$ terms) and analyzed using a natural orbital procedure. The possibility of optimizing molecular orbitals to describe the $^3, ^1\Pi$ 'resonances' using an iterative natural orbital procedure will be discussed.

Recently the radiative lifetime (τ) of the $a^1\Lambda$ state in NCl has been measured by two different experimental techniques with significantly different results, $\tau=1440$ ns and $\tau=2$ ns. To address this discrepancy calculations of the radiative lifetimes for the $(b^1\Sigma^+, a^1\Lambda) \rightarrow X^3\Sigma^-$ transitions in NCl have been

performed.³ Our results support the longer lifetime measurement.

If time permits we will discuss the application of recently developed computational techniques for the evaluation of first derivative nonadiabatic coupling matrix elements

$$g(J, I, R_\alpha, \tilde{r}) = \langle \Psi_J(\tilde{r}; \tilde{R}) | \frac{\partial}{\partial R_\alpha} \Psi_I(\tilde{r}; \tilde{R}) \rangle_{\tilde{r}}$$

using analytic gradient methods to discuss nonadiabatic chemical reactions.

In particular we will consider the charge exchange reaction



References:

- 1.(a) S. J. Havriliak and D. R. Yarkony, J. Chem. Phys. 83, 1168 (1985).
(b) D. R. Yarkony, J. Chem. Phys. 84, 2075 (1986).
2. M. Okamura, L. I. Yeh, D. Normand and Y. T. Lee, J. Chem. Phys. 85, 1971 (1986).
3. D. R. Yarkony, J. Chem. Phys. 86, 1642 (1987).

Spin Forbidden Radiative Processes

1. Change total spin angular momentum
Breit-Pauli Approximation

2. H^{SO} spin orbit hamiltonian

$$H^{SO} = h^{SO} + h^{SOO}$$

h^{SO} $1e^-$ spin orbit interaction

h^{SOO} $2e^-$ spin other orbit interaction

TODAY:

ELECTRONIC STATES ORIGINATING FROM

ELECTRON OCCUPATION

$$\sigma^2 \pi^2$$

STATES

$$2S+1 \Lambda_{\Omega}$$

'best' quantum number

point group: $C_{\infty v}$

$$b \ 1\Sigma^+_{0+}$$

$$a \ 1\Delta_2$$

$$x \ 3\Sigma^-_{1,0+}$$

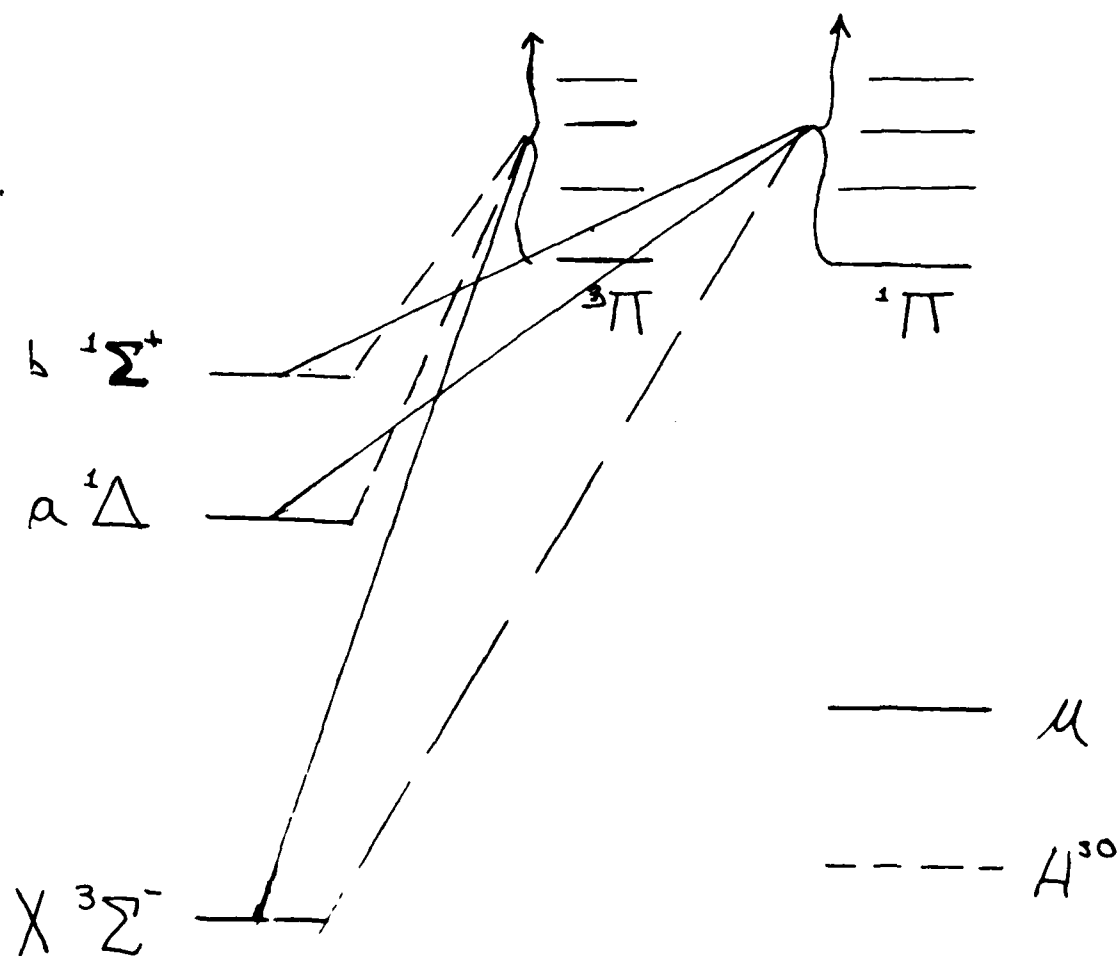
See "Spectra, lifetimes, and kinetics of matrix-isolated NI $b^1\Sigma^+$ and $a^1\Delta$ ",
J Chem Phys, 84, 2907(1986).

-----NEXT SLIDE-----

See "The lifetimes for spontaneous emission from the $X^3\Sigma^-(v=1)$ and $a^1\Delta$
states of CH^- ", J Chem Phys, 85, 1971(1986)

3. Mechanism

μ_1, μ_2



$$\psi(3\Sigma_1^-) = \psi^0(3\Sigma_1^-) + \psi^1(1\Pi_1, 3\Sigma_1^-)$$

$$\psi(1\Delta_2) = \psi^0(1\Delta_2) + \psi^1(3\Pi_2, 1\Delta_2)$$

$$\psi(1\Sigma_{0+}^+) = \psi^0(1\Sigma_{0+}^+) + \psi^1(3\Pi_{0+}, 1\Sigma_{0+}^+)$$

APPROACH

TWO UNIQUE FEATURES

1. SPACES: approach to treating Perturbation theory
2. SYMBOLIC MATRIX METHOD for treating H^{so}

States [Spectral Representation - Conventional]

$$\psi_I^1 = \sum_K \frac{\langle \psi_K^0 | H^{SO} | \psi_I^0 \rangle}{(E_I^0 - E_K^0)} \psi_K^0$$

ADVANTAGES

1. Facilitates incorporation of experimental data
2. Mixed representations

Spaces [SJH & DRY, J. Chem. Phys. 83, 1168 (1985)]

$$(H^0 - E_I^0) \psi_I^1 = - H^{SO} \psi_I^0$$

Advantages

1. AVOIDS (IMPOSSIBLE) TASK OF OBTAINING ALL ZEROth ORDER EIGENSTATES
2. PERMITS TREATMENT OF PROCESSES ORIGINATING IN COUPLING TO STATES EMBEDDED IN A CONTINUUM
3. ORBITAL OPTIMIZATION!

IN GENERAL

1. TRANSITION MOMENTS ARE SENSITIVE
to the QUALITY OF THE
WAVEFUNCTION
2. SPACE approach permits use of
a large CSF space

To exploit (2) with an eye to (1) we have
implemented

SYMBOLIC MATRIX METHOD for $H^{80} \psi^0$
DRY, J. Chem. Phys. 84, 2075 (1986)

CONCEPT:

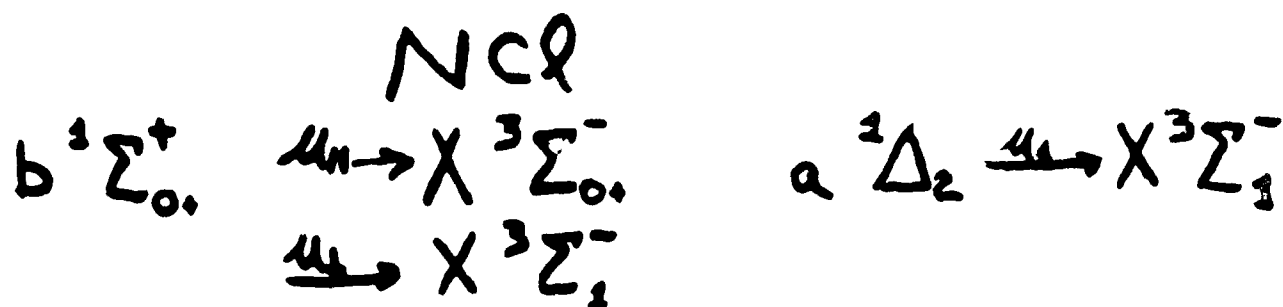
Representative MATRIX Elements

DIRECT PRODUCT SPACES

LIU & YOSHIMINE, J. Chem. Phys. 74, 612 (1981)

Benefits

- 1. AVOIDS SIZE LIMITATION OF CONVENTIONAL CI
10⁵ - 10⁶ CSF's 'routine'**
- 2. PERMITS MAXIMAL EXPLOITATION of SPACE METHOD**



$3,1\pi$ spaces $\sigma\pi^3$ valence orbitals

Method: 1 Orbitals: SA-MCSCF

$3\Sigma^-, 1\Delta, 1\Sigma^+, 3,1\pi$

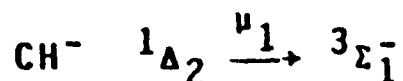
2. $\Psi^1(3\pi, a^1\Delta)$ $\Psi^1(3\pi, b^1\Sigma^+)$ $\Psi^1(\pi, X^3\Sigma^-)$
 $\Psi^1(1\Sigma^+, X^3\Sigma^-)$ $\Psi^1(1\Sigma^-, b^1\Sigma^+)$

DRY, J Chem Phys 86, 1042 (1987)

CABLE I. Spin-forbidden transition moments^a for $b \rightarrow X$ and $a \rightarrow X$ transition in NCl.

Reference	$\mu_{\parallel}(a^1\Delta, X^3\Sigma^-)$	$\mu_{\parallel}(b^1\Sigma^+, X^3\Sigma^-)$	$\mu_{\perp}(b^1\Sigma^+, X^3\Sigma^-)$
CVB [Ref. 4(a)]	0.174(-1)	0.153(-1) ^b	
Becker <i>et al.</i> (Ref. 5)	0.659(-3)		
Wayne-Colbourn (Ref. 6)		0.270(-2)	0.132(-2)
This work FO ^c 5000 cSF	0.330(-3)	0.921(-2)	0.407(-3)
SO 80000 cSF	0.507(-3)	0.924(-2)	0.441(-3)

^b Only total radiative rate measured < $\mu_{\parallel} \gg \mu_{\perp}$



Lengsfeld Jensen Yarkony

$3\Sigma^-$

1Δ

$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^2$ VALENCE States

3Π

1Π

$n_\sigma \rightarrow \pi \quad 1\sigma^2 2\sigma^2 3\sigma 1\pi^3$ VALENCE

$\pi \rightarrow \sigma^* \quad 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi$

$n_\sigma = 3\sigma \quad \sigma^* = 4\sigma \quad ?$

GOAL:

Construct $3,1\Pi$ space appropriate for ψ^1

STEP 1:

VARIATIONAL PRINCIPLE

$3\Sigma^-, 1\Delta, 3,1\Pi$ into State averaged MCSCF

RESULT:

4σ is very diffuse

$\text{CH}(^2\Pi) + e$

as expected

Step 2: (a) Construct $\psi^1(3\Pi, a^1\Delta)$

$\psi^1(1\Pi, \chi^3\Sigma^-)$

in flexible "2nd order space"
80,000 & 130,000 terms

(b) Analyze the solutions using
NATURAL ORBITALS

QUALITATIVELY:

$1\sigma^2 2\sigma^2 3\sigma 1\pi^3$ is correct

but

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma 1\pi$

 should be valence orbital

Step 3: Using 4σ NATURAL ORBITAL redo Step 2.

Conclusion: Now possible to optimize the space
used to describe the perturbation
in a manner analogous to that used
to optimize space for the zeroth
order wavefunction!

NO-A187 278

PROCEEDINGS OF THE HIGH ENERGY DENSITY MATTER (HEDM)
CONFERENCE HELD IN R. (U) AIR FORCE ASTRONAUTICS LAB
EDWARDS AFB CA W J LAUDERDALE ET AL. SEP 87

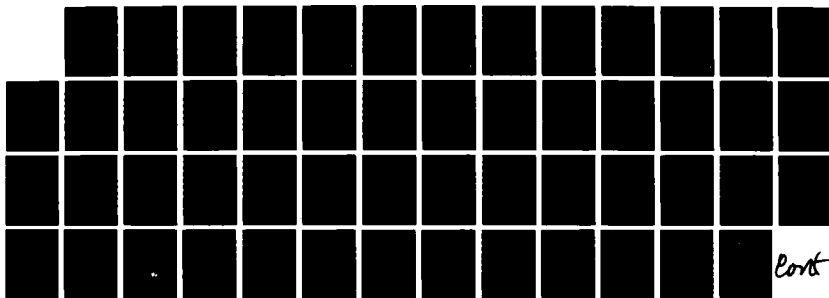
4/5

UNCLASSIFIED

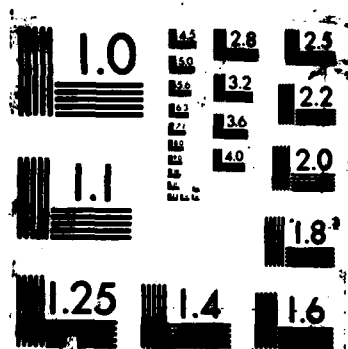
AFAL-CP-87-002

F/G 7/4

NL



Cont



Orbital Space

R = 2.00	MCSCF	NATORB 1	NATORB 2
E(3 Σ^-)	au	-38.4303168	-38.4334322
E(1 Δ)	qu	-38.3989635	-38.4008761
$\Delta E(3\Sigma^- - 1\Delta)$	cm ⁻¹	6881	7145
E(2)(3 Σ^- , 1 Π)	cm ⁻¹	0.7530(-2)	0.7956(-2)
E(2)(1 Δ , 3 Π)	cm ⁻¹	0.1555(-2)	0.1573(-2)
$\nu(1\Delta, 3\Sigma^-)$	au	0.622(-3)	0.398(-3)
"T"	s	3.9	8.5

$$T^{-1} = 2.0261 \times 10^{-6} \cdot \sigma^3 \cdot \mu^2$$

EXPERIMENTAL STUDIES ON THE SYNTHESIS OF NEW NOBLE GAS FLUORIDES AND HIGH OXIDATION STATE ENERGETIC FLUORINE COMPOUNDS INVOLVING UNUSUAL BONDING SITUATIONS

W. W. WILSON AND K. O. CHRISTE

ROCKETDYNE DIVISION OF ROCKWELL INTERNATIONAL, CANOGA PARK, CA 91303

The primary objective of this program is to demonstrate the feasibility of synthesizing hypervalent, high oxidation state fluorides of nitrogen, oxygen and noble gases. Typical target compounds are NF_4 , OF_4 and ArF_2 .

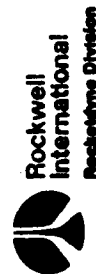
Our initial efforts are concentrated on the synthesis of NF_5 . A sapphire reactor was set up for uv-photolysis in liquid F_2 at -196° . The efficiency of the apparatus was demonstrated by preparing $\text{NF}_4^+\text{BF}_4^-$ from $\text{NF}_3 + \text{F}_2 + \text{BF}_3$, but photolysis of $\text{NF}_3 + \text{F}_2$ alone did not produce detectable amounts of NF_5 or NF_4^+F^- . A matrix isolation apparatus was built and the $\text{NF}_3\text{-F}_2\text{-BF}_3$ system was studied in Ar matrix at 5°K using uv-photolysis. Since no evidence for the formation of either any new species or $\text{NF}_4^+\text{BF}_4^-$ was obtainable under these conditions, the apparatus was modified to use microwave discharge instead of uv-photolysis for the generation of F atoms. This method has the advantages of producing much higher F atom concentrations without photolytically destroying the desired products. The efficiency of the system was demonstrated for the $\text{O}_2\text{-F}_2$ system producing the known O_2F radical in good yields. The reactions of microwave discharged generated F atoms with either NF_3 or BF_3 alone in Ar matrix so far have not generated detectable amounts of any new species.

Preliminary experiments using ^{18}F radio tracer studies were carried out to determine whether nitrogen can exhibit a coordination number of five with fluorine. Unfortunately, the facilities available (at the University of Glasgow) did not permit the generation of sufficiently large amounts of the $^{18}\text{F}_2$ required for our experiments.

EXPERIMENTAL STUDIES ON THE SYNTHESIS OF NEW NOBLE GAS
FLUORIDES AND HIGH OXIDATION STATE ENERGETIC FLUORINE COMPOUNDS
INVOLVING UNUSUAL BONDING SITUATIONS

W. W. WILSON AND K. O. CHRISTE
ROCKETDYNE DIVISION OF ROCKWELL INTERNATIONAL, CANOGA PARK, CA

- OBJECTIVES
 - ACHIEVE ENERGY INCREASE BY UNUSUAL BONDING SITUATIONS
SUCH AS HYPERVALENCY
 - PREPARE AND CHARACTERIZE NEW HYPERVALENT FLUORIDES OF
NITROGEN, OXYGEN AND THE LIGHTER NOBLE GASES



HYPERVALENCY

- DEFINITION

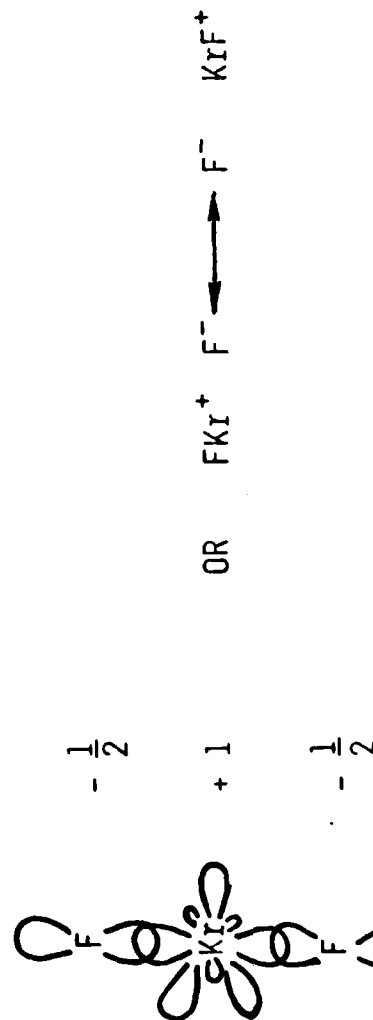
IN HYPERVALENT COMPOUNDS THE NUMBER OF VALENCE ELECTRONS ON CENTRAL ATOM EXCEEDS 8

- TYPICAL EXAMPLE



FREE VALENCE ELECTRON PAIRS (VEP) ON Kr WANT AS MUCH S-CHARACTER AS POSSIBLE

THIS CAN BE ACHIEVED BY FORMATION OF SEMI-IONIC 3-CENTER 4-ELECTRON BONDS FOR THE TWO Kr-F BONDS



HYPERVALENCY (Continued)

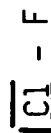
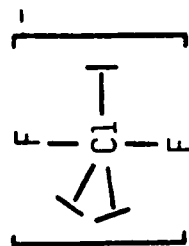
• RESULT

HYPERVALENT SEMI-IONIC 3c-4e BONDS POSSESS ABOUT HALF THE BOND STRENGTH OF A NORMAL COVALENT BOND



$f \text{ (MDYN/\AA)} \quad 2.46$

3.55



$f \quad 2.3$

4.4

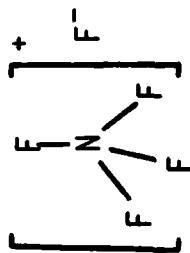
WEAKENING OF THE BONDS WILL INCREASE THE ENERGY CONTENT OF A MOLECULE

• TYPICAL HYPERVALENT TARGET COMPOUNDS

NF₅, OF₄, ArF₂

NF₅ CHEMISTRY

- NF₅ COULD EXIST IN COVALENT OR IONIC FORM



ENERGY DIFFERENCE ~ 102 KCAL/MOL

- CALCULATED ΔH_f OF NF₅ = 71 KCAL/MOL
- THEORETICAL PERFORMANCE CALCULATIONS
 - I_{VAC} (50 PSI, ϵ = 100) FOR NF₅-H₂ SYSTEM = 505 SEC
 - F₂-H₂ SYSTEM = 487 SEC

NF₅ CHEMISTRY. EXPERIMENTAL STUDIES

- UV-PHOTOLYSIS AT -196°C IN LIQUID F₂ IN SAPPHIRE REACTOR USING
1 KW FOCUSED HIGH-PRESSURE Hg ARC WITH H₂O-PYREX FILTER

MODEL REACTION SUCCESSFUL



BUT ATTEMPTED NF₅ SYNTHESIS

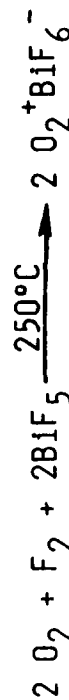


DID NOT PRODUCE ANY NEW PRODUCT STABLE AT -186°C

RESIDUE AFTER NF₃ AND F₂ REMOVAL AT -186°C

WAS TRACE OF O₂F₂ (O₂ + F₂ $\xrightarrow{h\nu}$ O₂F₂)

PURIFICATION OF F₂



NF₅ CHEMISTRY. EXPERIMENTAL STUDIES

- UV-PHOTOLYSIS IN N₂ MATRIX (MR = 300) AT 10°K

SYSTEMS STUDIED

NF₃, F₂, BF₃

NF₃-F₂, BF₃-F₂

NF₃-F₂-BF₃

NO NEW SPECIES OBSERVED

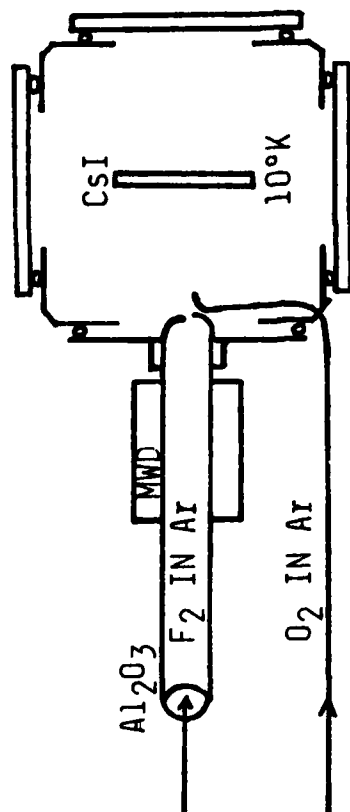
POSSIBLE PROBLEMS

F CONCENTRATION TOO LOW

DESIRED PRODUCTS DESTROYED BY PHOTOLYSIS

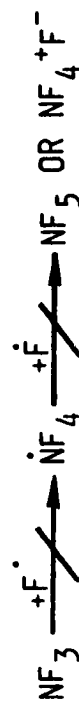
NF₅ CHEMISTRY. EXPERIMENTAL STUDIES

- GENERATION OF \dot{F} ATOMS BY MICROWAVE DISCHARGE TECHNIQUE AND APPARATUS SIMILAR TO THAT OF DR. JACOX



APPARATUS TESTED FOR $O_2 + \dot{F}$ REACTION IN Ar (\sim JACOX)
 $O_2\dot{F}$ FORMED IN GOOD YIELD

SYSTEMS STUDIED SO FAR



ROCKWELL INTERNATIONAL
 ROCKETDYNE DIVISION
 6633 Canoga Ave./Canoga Park, CA 91304

NF₅ CHEMISTRY. EXPERIMENTAL STUDIES

- CONCLUSION

NO EXPERIMENTAL EVIDENCE FOR FORMATION OF EITHER
COVALENT NF₅ OR IONIC NF₄⁺F⁻ FROM NF₃ AND F[•]
AT TEMPERATURES AS LOW AS 10°K

- TWO FUNDAMENTAL QUESTIONS

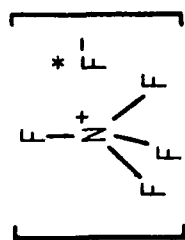
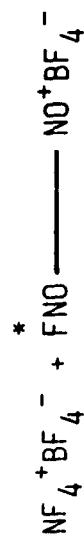
- NF₅: CAN NITROGEN COORDINATE 5 FLUORINES?

- NF₄⁺F⁻: HOW EASILY WILL F⁻ ABSTRACT AN F[•] FROM NF₄⁺
TO GIVE NF₃ + F₂?

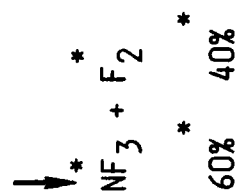
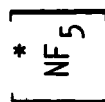
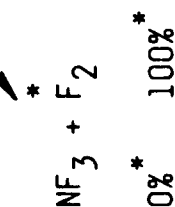
- POSSIBLE ANSWER FROM ¹⁸F RADIO TRACER STUDIES

NF₅ CHEMISTRY. ¹⁸F RADIO TRACER STUDY

- DISPLACEMENT REACTION



IF CN_{MAX} = 4



- DISTRIBUTION OF ¹⁸F IN PRODUCTS SHOULD CONCLUSIVELY SHOW WHETHER COVALENT NF₅ CAN EXIST OR NOT

NE₅ CHEMISTRY. ¹⁸F RADIO TRACER STUDY

- DISPLACEMENT REACTION BETWEEN NF₄BF₄ AND FNO WAS DEMONSTRATED FOR ¹⁹FNO
- RADIO TRACER EXPERIMENTS WERE ATTEMPTED BY PROF. WINFIELD (UNIV. OF GLASGOW)
- DIFFICULTIES WITH PRODUCTION OF SUFFICIENT AMOUNTS OF ¹⁸F₂ FROM Cs¹⁸F FOR
$$(2\text{NO} + {}^{18}\text{F}_2 \longrightarrow 2{}^{18}\text{FNO}) \quad (t_{\frac{1}{2}} {}^{18}\text{F} = 110 \text{ MIN})$$
- HAD BEEN WAITING FOR REPAIR OF ACCELERATOR AT UC IRVINE FOR ²⁰Ne(d,α) ¹⁸F OR ¹⁹F (γ, n) ¹⁸F REACTIONS
- EXPERIMENT WILL BE RESUMED IN COLLABORATION WITH DR. SCHROBILGEN AT MCMASTER UNIVERSITY

ROCKWELL INTERNATIONAL
ROCKETDYNE DIVISION
8033 Carnegie Ave./Carnegie Park, CA 91304

PLANNED WORK

- COMPLETION OF MATRIX ISOLATION STUDY AND RADIO TRACER STUDY OF NF_5
- SYNTHESIS OF $\text{ArF}^+\text{PtF}_6^-$ AND ArF_2
- SYNTHESIS OF $\text{OF}_3^+\text{PtF}_6^-$ AND OF_4

1st HIGH ENERGY DENSITY MATTER CONFERENCE
Department of the Air Force - AF Rocket Propulsion
May 12 and 13 1987, Arlington, Virginia

Contract

NEW HIGH ENERGY DENSITY SMALL RING SYSTEMS

Presentation

THE PREVALENCE OF RHOMBIC STRUCTURES IN A_2B_2 TETRAATOMICS

by KOOP LAMMERTSMA AND OSMAN F. GUNER

Dept. of Chemistry, University of Alabama at Birmingham,
University Station 219 PHS, Birmingham, AL 35294.

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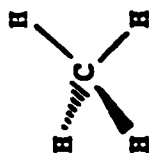
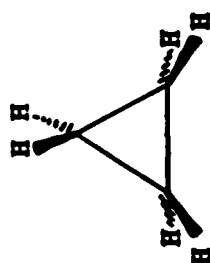
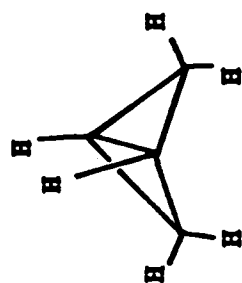
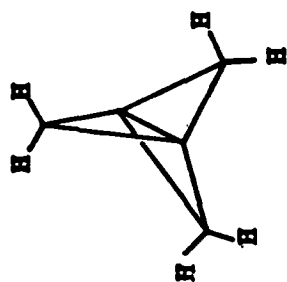
THE PREVALENCE OF RHOMBIC STRUCTURES IN A_2B_2 TETRAATOMICS

by KOOP LAMMERTSMA AND OSMAN F. GUNER, Dept. of Chemistry, University of Alabama at Birmingham, University Station 219 PHS, Birmingham, AL 35294.

A variety of reactive solid state materials contain rhombic building blocks as important structural ingredients. Illustrative are the formel $Al_2Si_2^{2-}$ and $Li_2X_2^-$ ($X = N, P, As$) fragments in the Zintl' complexes $CaAl_2Si_2$ and MLi_2X_2 ($M = Ce, Zr, Pr$), respectively, whereas the formel $Be_2Ge_2^{2-}$ part in $CaBe_2Ge_2$ can be viewed as a square network. These building blocks are tetraatomic structures of the A_2B_2 -type. We have studied by ab initio MO theory a variety of 10, 12, 14, and 16 valence electron A_2B_2 species to determine whether high energy density rhombic structures are preferred at the molecular level.

For the 16 el. species C_4 , C_3HB , $C_2H_2B_2$, and related cations, the rhombic structures are indeed minima on the potential energy surface. This is also the case for the 14 el. C_3Be , C_3HBB_e , and related cations. However, for the 12 el. C_2Be_2 the linear form (triplet) is more stable than the rhombic isomer, which is a minimum energy structure.

In our full potential energy search on the limiting 12 el. $C_2Li_2^{2-}$ and 10 el. B_2B_2 species we focus on the prevalence of the highly energetic rhombic structures and their unique bonding properties. Similarly, preliminary data on the 16 el. disilicondicarbide C_2Si_2 will be presented.

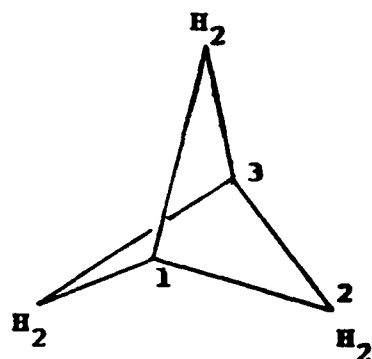


INVERTED GEOMETRIES AT CARBON



"inverted" sp^3

sp^3



6-31G* Geometry

C_1-C_3 1.543 Å

C_1-C_2 1.502 Å

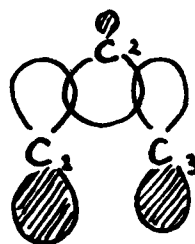
No electron density between C_1 and C_3

The HOMO (I) is a non-bonding σ -orbital

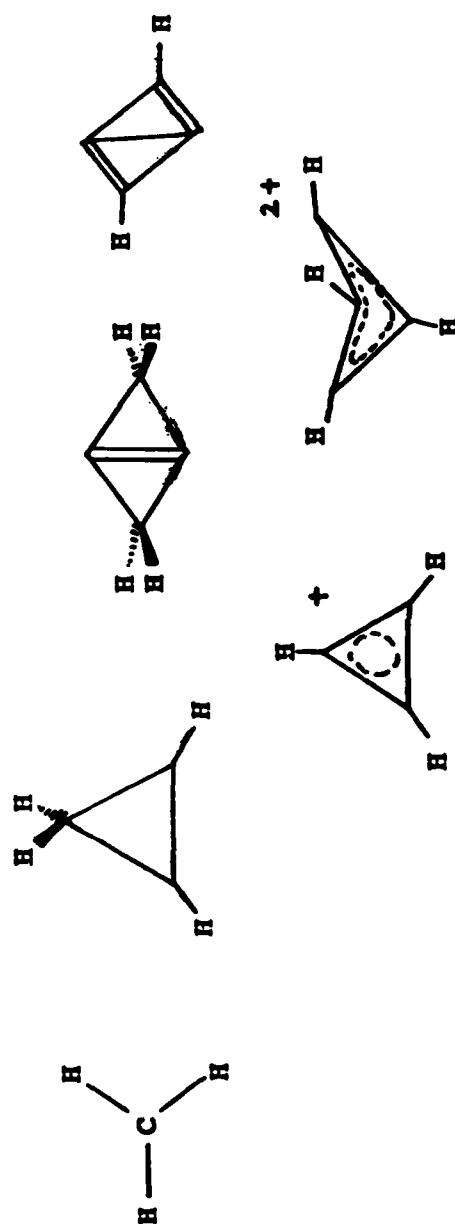
The short distance between C_1 and C_3 results from two σ -bridged- π -bonding orbitals (II)



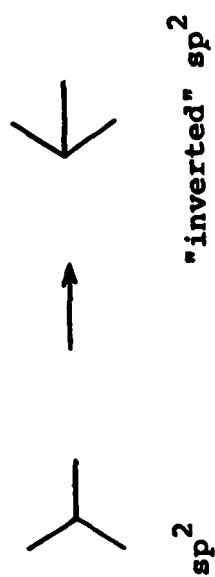
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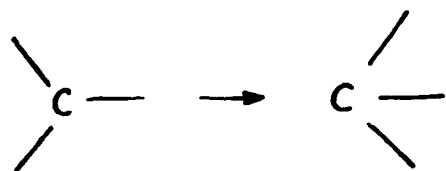


II

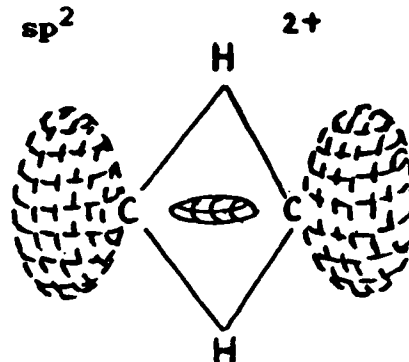


INVERTED GEOMETRIES AT CARBON

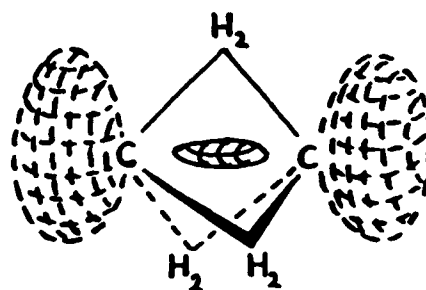
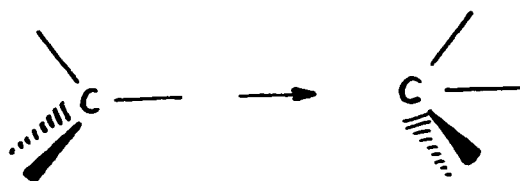




INVERTED sp^2

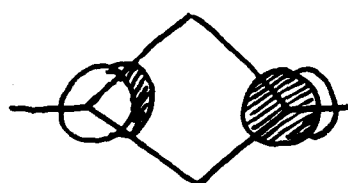
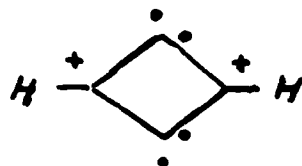


INVERTED sp^3

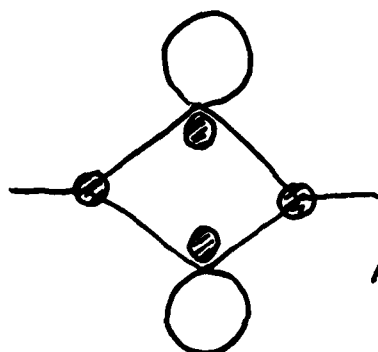


σ Deficient bonding

IMPORTANT MO's

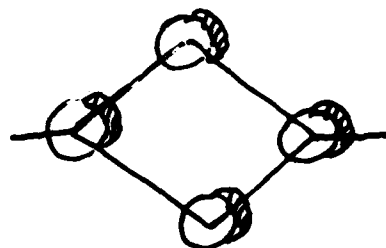


LUMO



HOMO

NON-BONDING σ



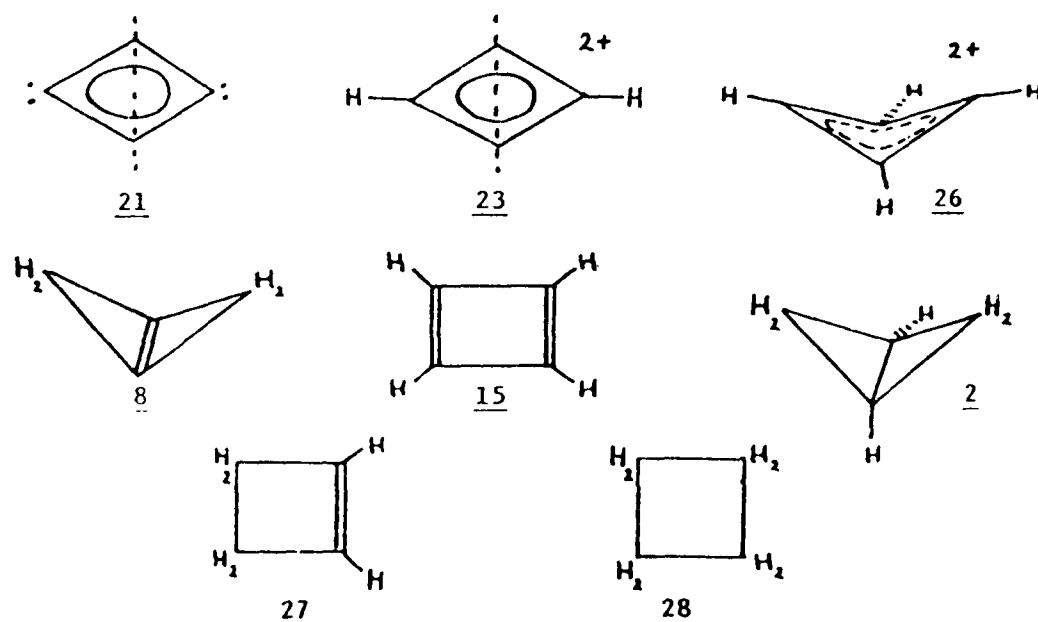
BONDING π

4C - 2E 'AROMATIC'

Table 1. 6-31G* energies (in au), heats of formation (ΔH_f , in kcal/mol), and strain energies (SE, in kcal/mol) for four-membered ring structures.

compound	formula	energy	ΔH_f	SE
21 ²⁹	C ₄	-151.14598	228	
23 ²⁹	C ₄ H ₂ ²⁺	-151.53998	726	
Cyclobutadiene dication (26) ³⁵	C ₄ H ₄ ²⁺	-152.91650	623	
Bicyclo[1.1.0]butene (8) ¹⁴	C ₄ H ₄	-153.58016	142	127
1,3-Cyclobutadiene (15) ²³	C ₄ H ₄	-153.6412	103	65
Bicyclo[1.1.0]butane (2) ¹⁴	C ₄ H ₆	-154.87176	51.9	65
Cyclobutene (27) ^{9g}	C ₄ H ₆	-154.89962	37.5	29
Cyclobutane (28) ^{9g}	C ₄ H ₈	-156.09703	6.8	26
Hydrogen ¹⁴	H ₂	-1.12683		

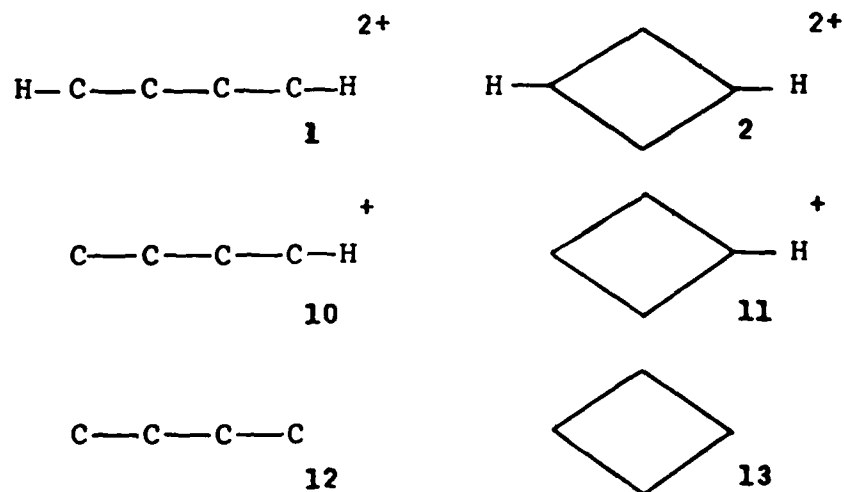
Enthalpies given to the nearest tenth are experimental data, integer values are based on calculated energies. The strain energy, SE, are derived from Franklin group equivalents: CH₂=-4.93, CH=0.80, cis-CH=CH=18.88, and C=C=24.57 kcal/mol.

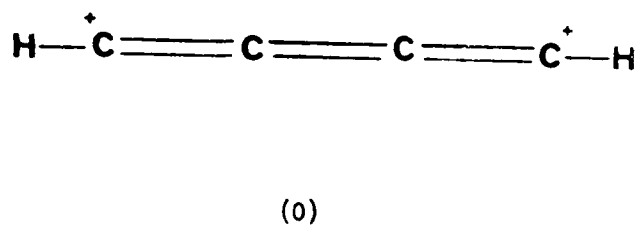
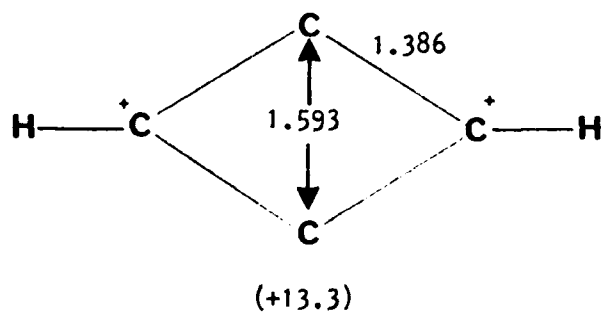
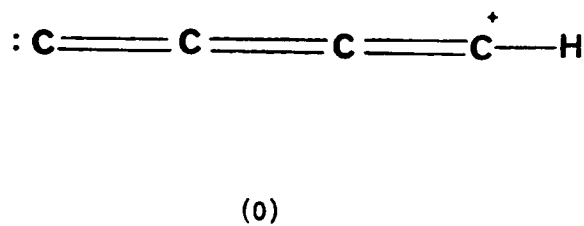
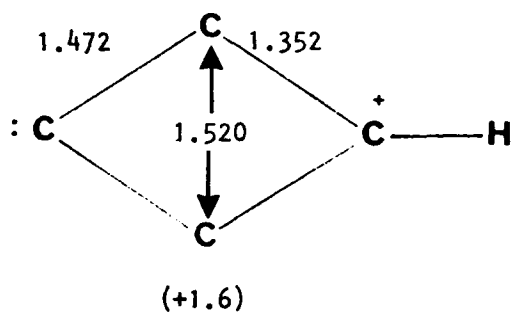
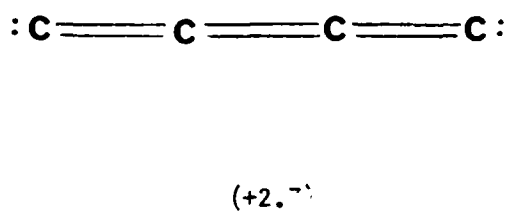
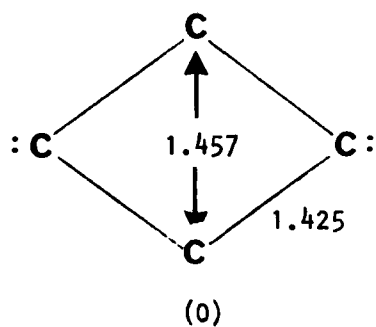


Relative (in kcal/mol) Energies of $C_4H_2^{2+}$, C_4H^+ ,
and C_4 Isomers.

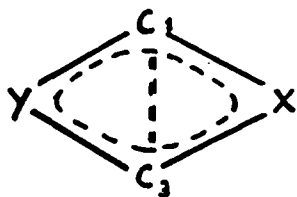
Structures		HF/ 6-31G*	MP2/ 6-31G*	MP3/ 6-31G*
1	$D_{\infty h}$	0.0	0.0	0.0
2	D_{2h}	48.1	-1.5	13.3
10 ^a	$C_{\infty h}$	0.0	0.0	0.0
11	C_{2v}	36.3	-13.0	0.2
12	$D_{\infty h}$	0.0	0.0	0.0
13	D_{2h}	23.7	-14.6	-2.7

^a HF/3-21G geometry





ENERGIES AT MP3/6-31G* (kcal/mol)

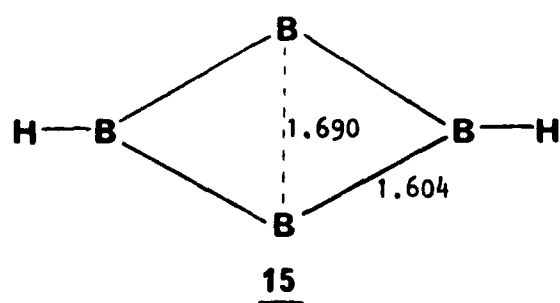
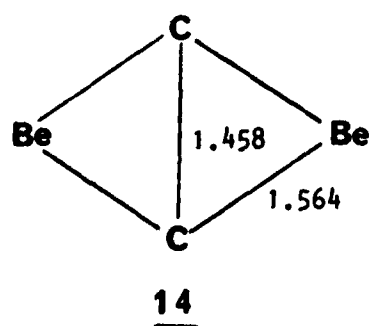
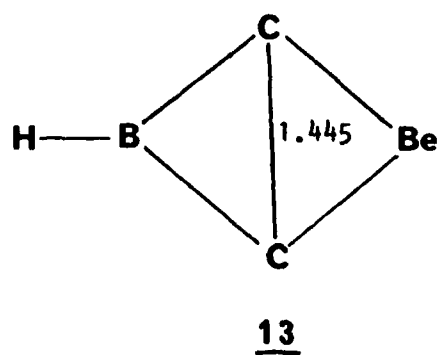
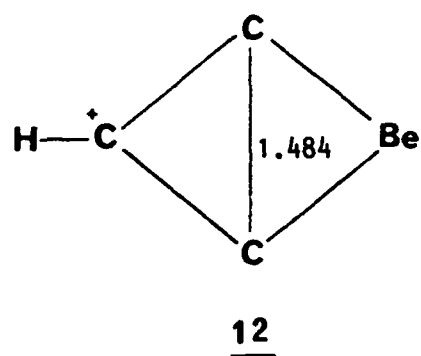
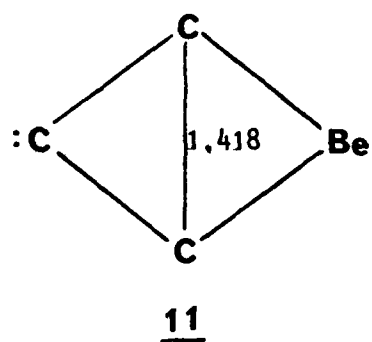
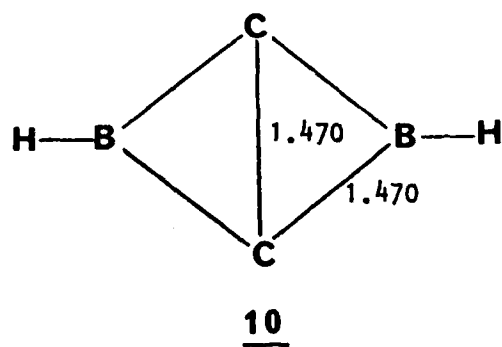
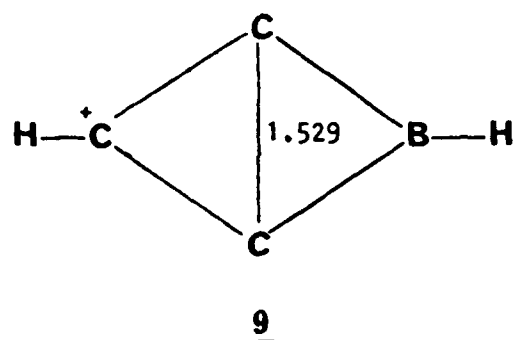
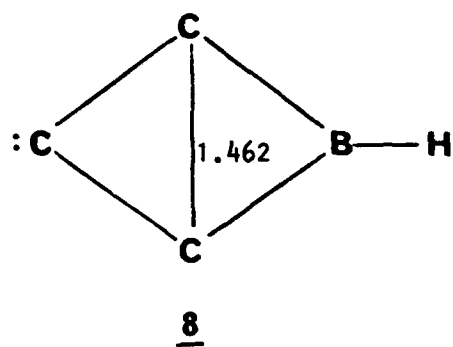


<u>5</u>	X=Y=C	<u>11</u>	X=Be; Y=C
<u>6</u>	X=CH ⁺ ; Y=C	<u>12</u>	X=Be; Y=CH ⁺
<u>7</u>	X=Y=CH ⁺	<u>13</u>	X=Be; Y=BH
<u>8</u>	X=BH; Y=C	<u>14</u>	X=Y=Be
<u>9</u>	X=BH; Y=CH ⁺	<u>15</u>	X=Y=BH; C=B
<u>10</u>	X=Y=BH		

Table 1. 6-31G* Energies, Structural Parameters, and Mulliken Overlap Population Analysis for the Four-Membered Structures 5-15.

compound	energy	geometry		overlap population
		r(C ₁ -C ₃)	r(C-X), r(C-Y)	
<u>5</u> , ^a C ₄	-151.14598	1.457	1.425	-0.063
<u>6</u> , ^a C ₄ H ⁺	-151.45693	1.520	1.352, 1.472	-0.013
<u>7</u> , ^a C ₄ H ₂ ²⁺	-151.53998	1.593	1.386	-0.236
<u>8</u> , C ₃ BH	-138.65329	1.462	1.479, 1.418	0.138
<u>9</u> , C ₃ BH ₂ ⁺	-139.01220	1.529	1.526, 1.345	0.060
<u>10</u> , C ₂ B ₂ H ₂	-126.15541	1.470	1.470	0.330
<u>11</u> , C ₃ Be	-127.98366	1.418	1.563, 1.421	0.219
<u>12</u> , C ₃ BeH ⁺	-128.39388	1.484	1.619, 1.345	0.107
<u>13</u> , C ₂ BBH	-115.47831	1.445	1.558, 1.473	0.389
<u>14</u> , C ₂ Be ₂	-104.79129	1.458	1.564	0.495
<u>15</u> , B ₄ H ₂	-99.72164	1.690 ^b	1.604 ^b	0.306

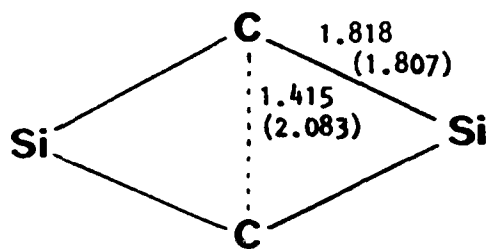
^a Reference 8. ^b The respective r(B-B) bonds are given.



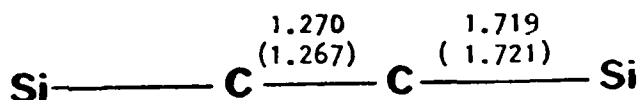
See "Site Preferences and Bond Length Differences in CaAl_2Si_2 -Type Zintl Compounds", J Am Chem Soc, 108, 1876(1986).

-----NEXT SLIDE-----

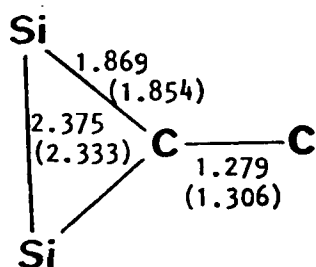
See reference from previous slide, but page 1884.



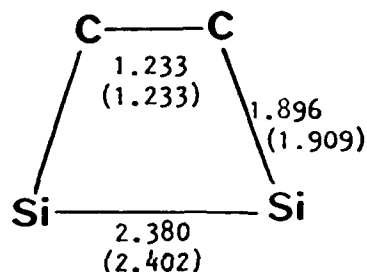
1s 0.00 (0.00) (0)
1t -- (86.06) (0)*



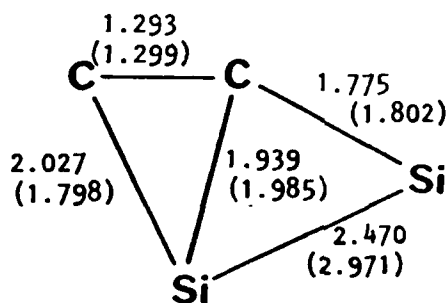
2s 23.67 (22.33) (0)
2t 15.87 (0.02) (0)



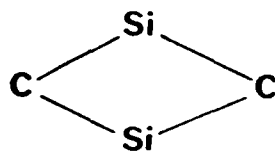
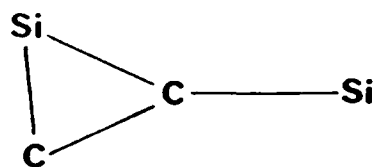
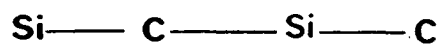
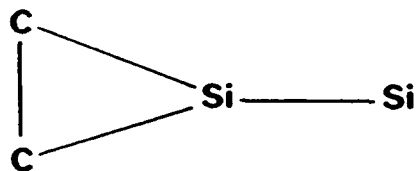
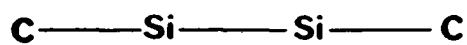
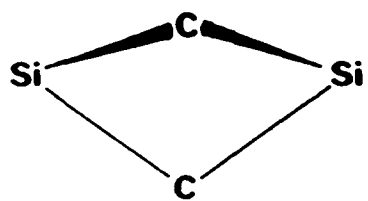
3s 41.42 (29.82) (2)
3t -- (30.43) (0)*

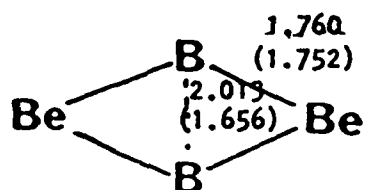


4s 51.14 (94.71) (2)
4t -- (48.58) (1)



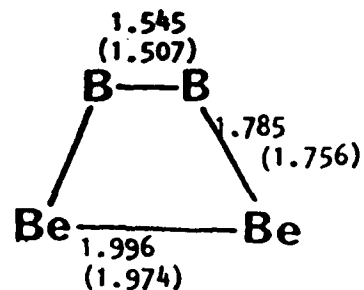
5s -- (9.45) (0)*
5t -- (12.95) (0)*





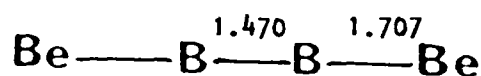
1s 33.48 (20.80) (0)

1t 0.00 (0.00) (1)

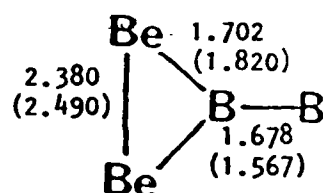


2s 27.36 (11.75) (0)

2t 11.69 (4.34) (2)

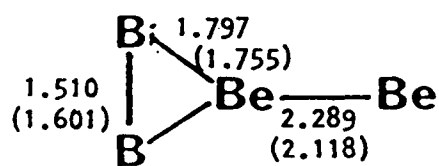


3s 41.45 (59.80) (2)



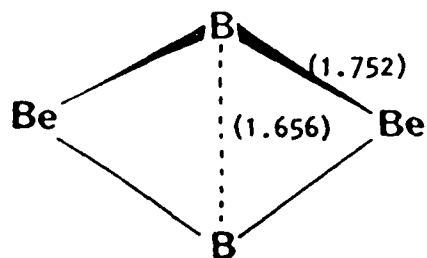
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4t 58.89 (-1.48) (1)

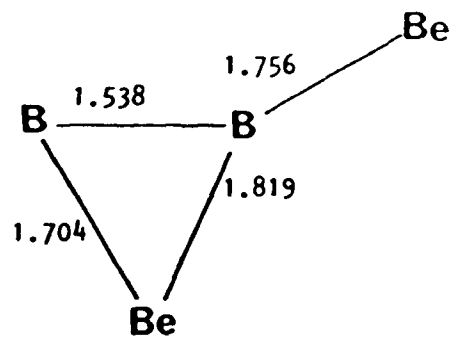


5s 37.31 (43.28) (0)

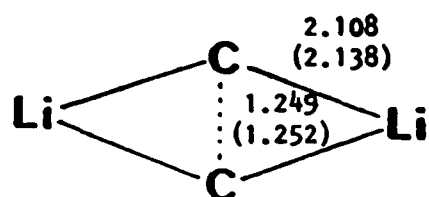
5t 70.12 (30.65) (1)



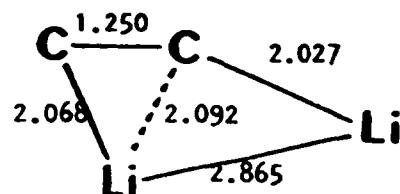
6t 1.39 (-0.06) (0)



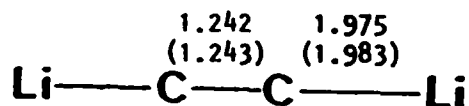
7s 11.09 (24.56) (1)



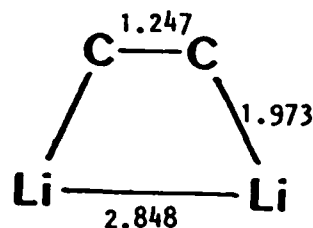
1s 13.62 (46.15) (0)
1t 0.24 (0.21) (1)



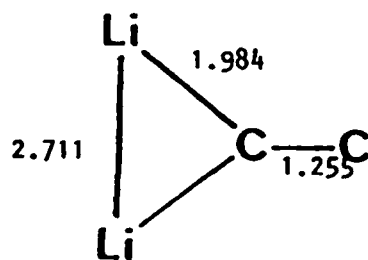
2s 20.60 (33.54) (0)



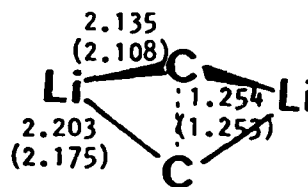
3s 9.42 (44.59) (0)
3t 0.04 (-2.66) (0)



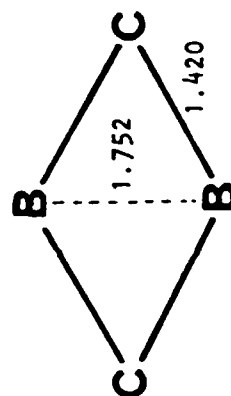
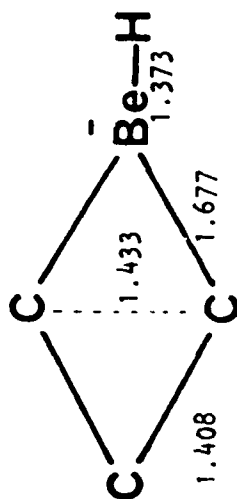
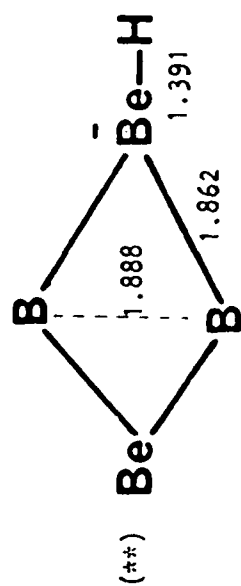
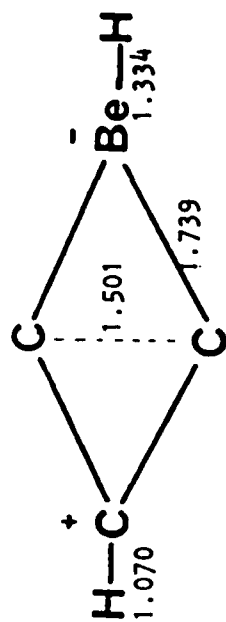
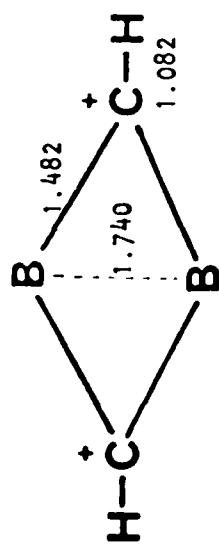
4s 24.44 (37.46) (2)



5s 29.79 (39.92) (2)



6s 20.18 (35.97) (0)
6t 0.00 (0.00) (0)



PHOTOEXCITATION OF TRIATOMIC HYDROGEN

H. Helm and L. J. Lembo

**Molecular Physics Department
SRI International, Menlo Park, Ca 94025**

- 1. Emission Spectra (Herzberg)**
- 2. Formation of H_3 in Charge Transfer**
- 3. Photoionization Spectra**
- 4. Two - Photon Ionization**
- 5. Excited - State Charge Transfer**
- 6. Future Work**

**Supported by the Air Force Office of Scientific Research
under Contract FQ8671-8700 432**

ABSTRACT

Submitted to
The First Annual High Energy Density Matter Conference
(12-13 May) 1987, Rosslyn Virginia

PHOTOEXCITATION OF TRIATOMIC HYDROGEN*

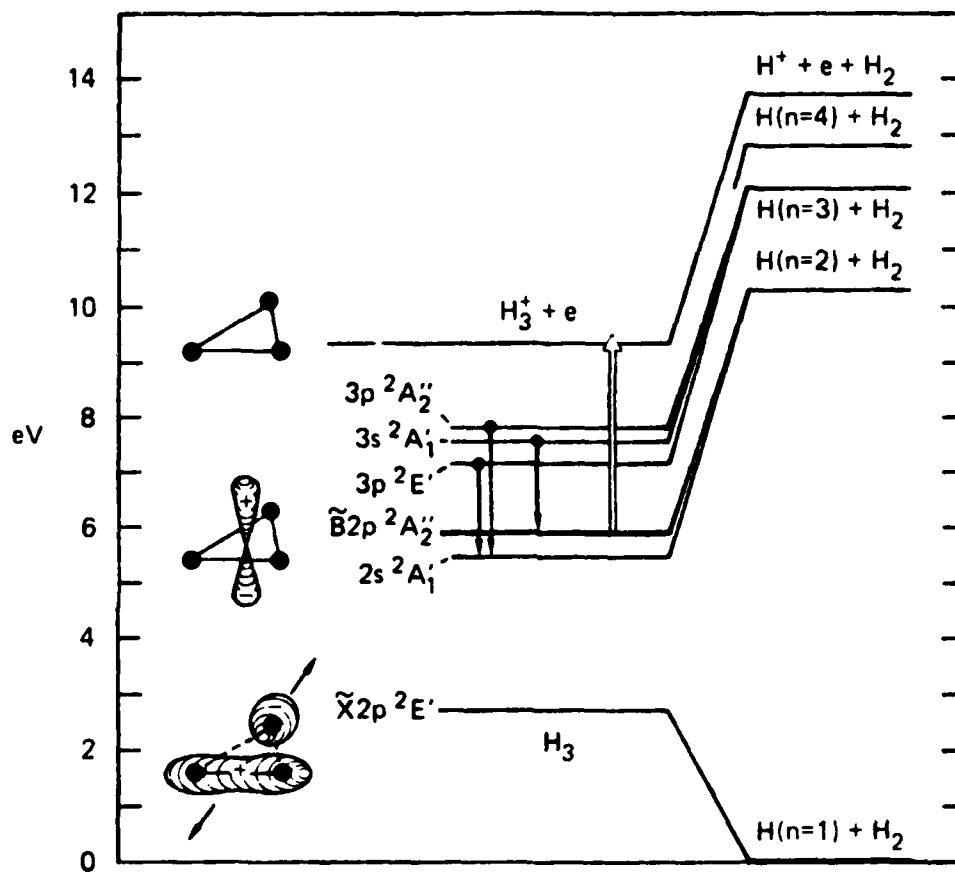
H. Helm, and L. J. Lembo
Molecular Physics Department
SRI International Menlo Park, Ca 94025.

We have used a coaxial laser fast-neutral-beam spectrometer to study photoabsorption of long-lived species of H_3 . The H_3 molecules are formed by electron transfer from cesium to mass-selected H_3^+ . The neutral molecules are detected by photoionization several microseconds after their formation. Single-photon ionization of H_3 has been observed in the near UV (3620 to 3380 Å) via autoionizing Rydberg states. In addition one-photon resonant two-photon ionization has been observed via the $3d^2A_1'$ state at 5781 Å. The photoionization data suggest that the long lived H_3 species are molecules in the previously known $2p^2A_2''$ state. We will discuss these results and our current understanding of the structure of this triatomic hydrogen species.

* Work supported by the Air Force Office of Scientific Research.

MP No. 87-085

Energy Diagram



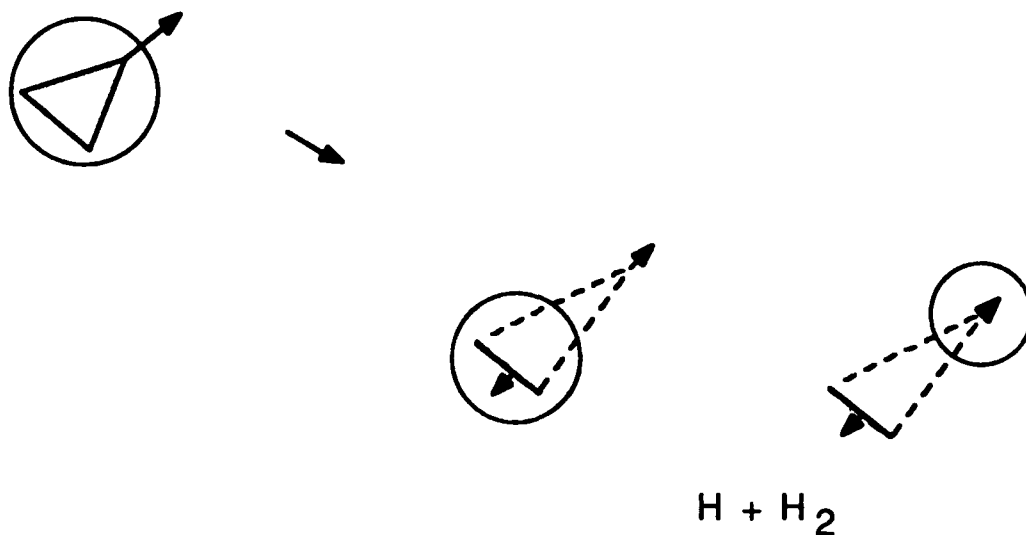
Three of the Emission bands observed by Herzberg and coworkers are shown by the full arrows. (Ref. 1-5)

The photoionization step from the metastable H_3 state is shown by the open arrow. (Ref. 6).

Predissociation of $n=2$ states

$2s\ A'_1$

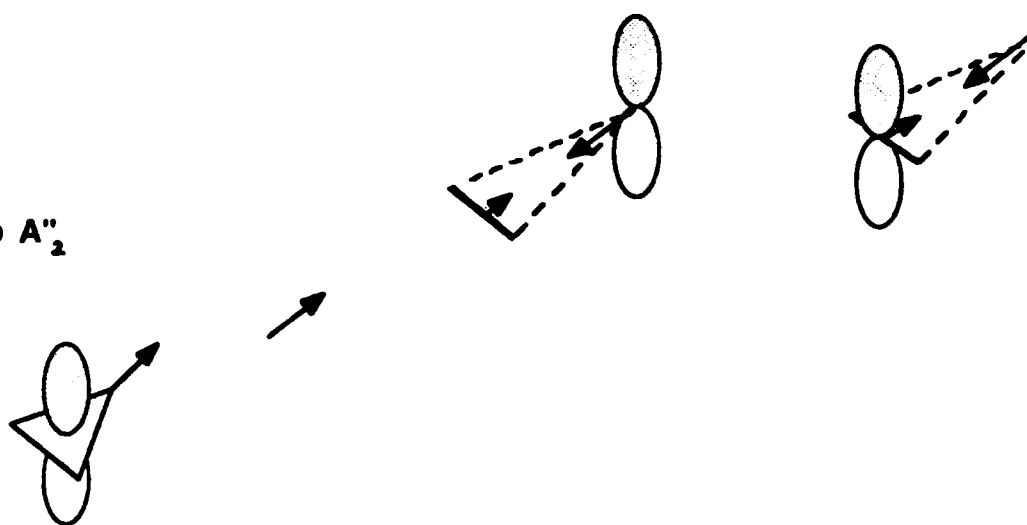
vibrational coupling



$2p\ A''_2$

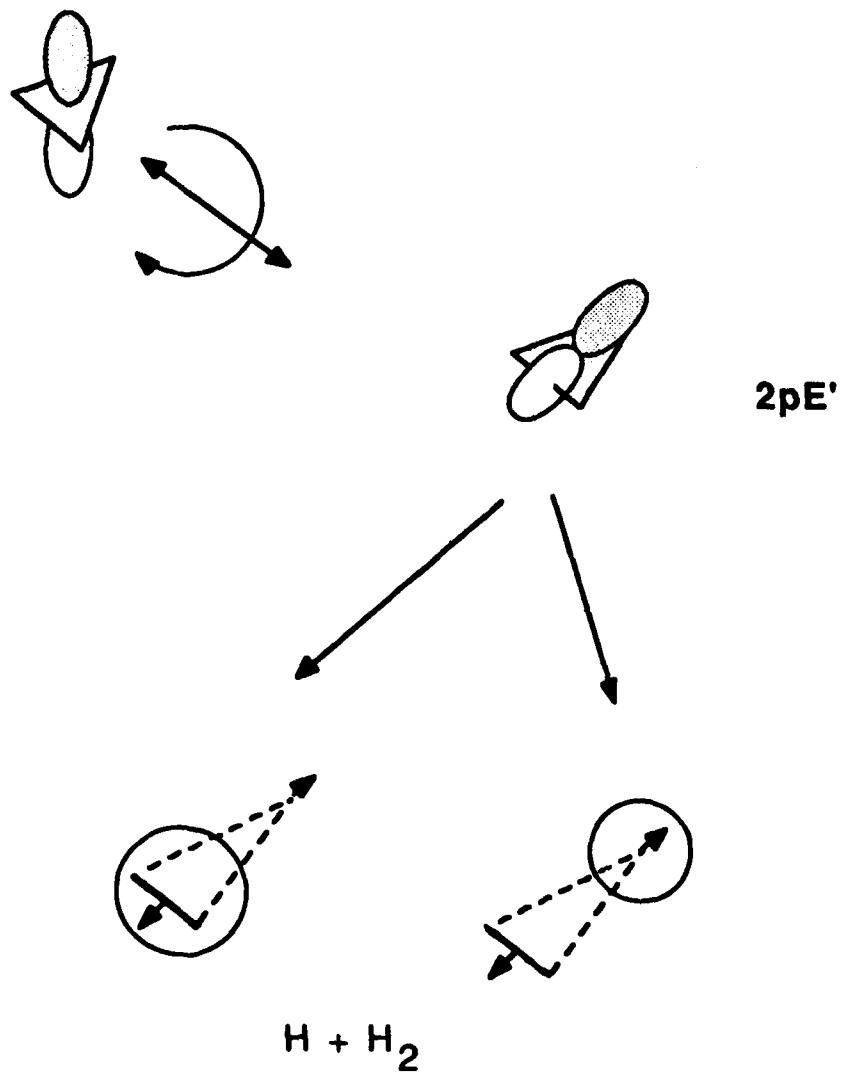
$H_2 + H(2p)$

$H_2^* + H$



Predissociation of $n=2$ states

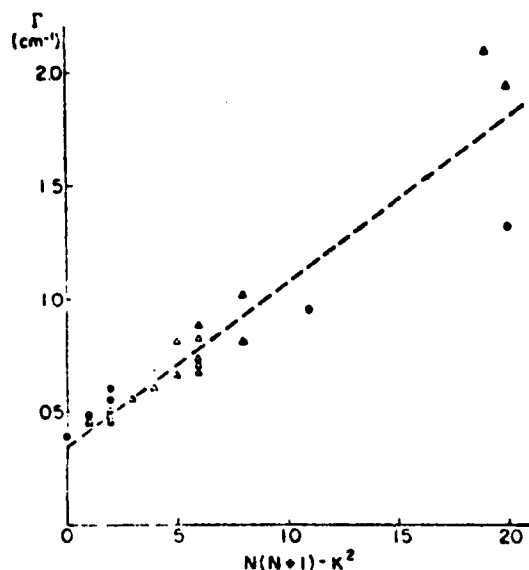
$2p\ A_2''$ Rotational coupling



Metastable triatomic hydrogen

Lifetime of $2pA''_2$ state depends on the degree of rotation of the molecule

(Herzberg, Hougen and Watson, Ref.5)

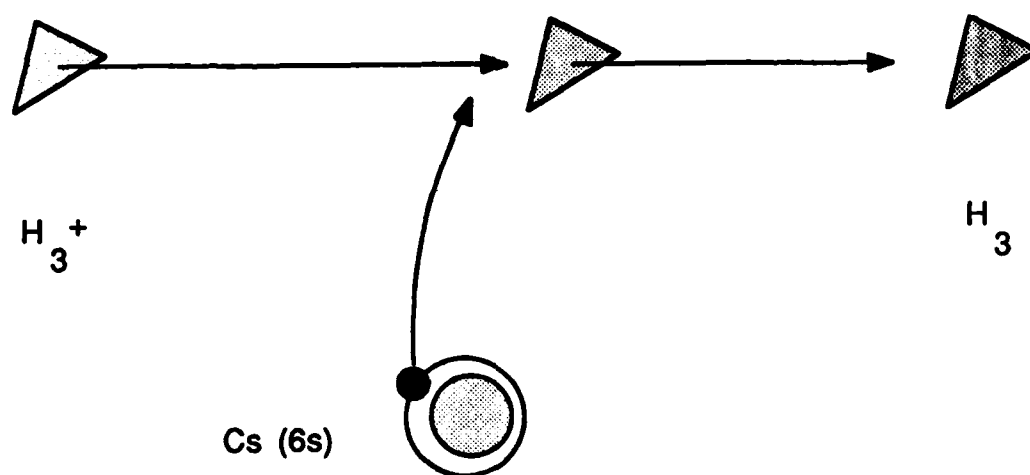


The residual width of the lowest level ($N=0, K=0$)

is attributed to Doppler Broadening

Radiative lifetime for $2pA''_2 - 2sA'_1$ transition (1090 cm^{-1})
has been calculated to be 87 us (Gellene and Porter, Ref.7)

Formation of H_3 by Charge Transfer

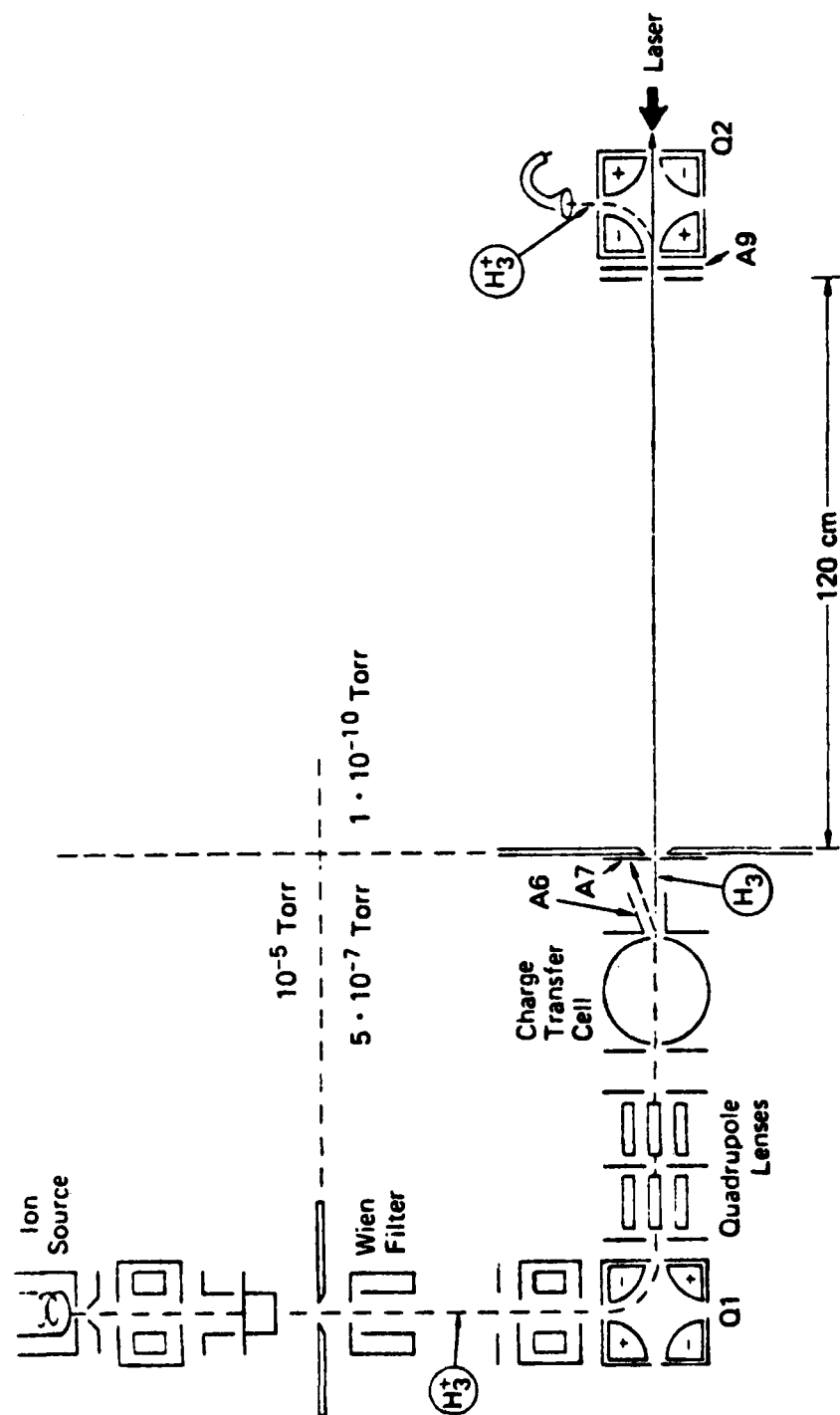


Ionization Potential of Cs : 3.89 eV

Binding Energy of $n=2$ Electron to H_3^+ $\sim Ry/4$

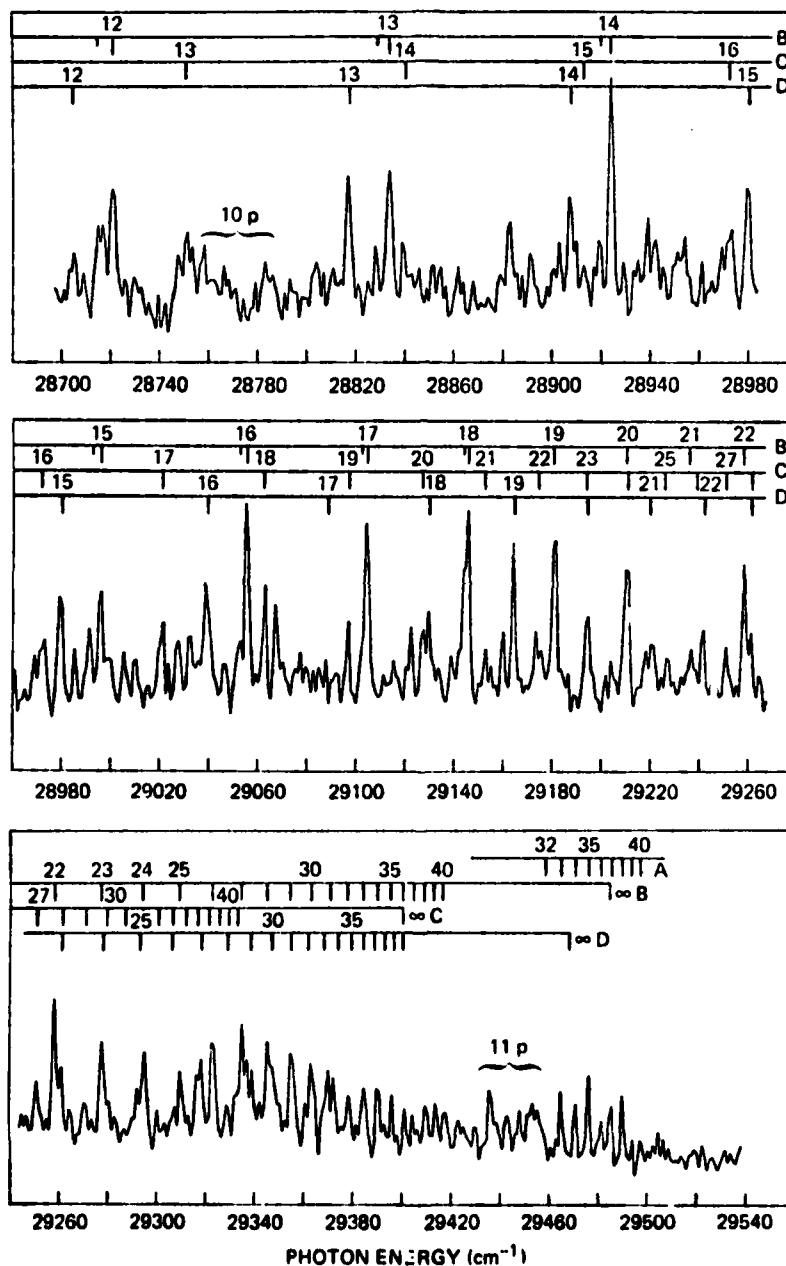
References 7-13

Photoionization Experiment



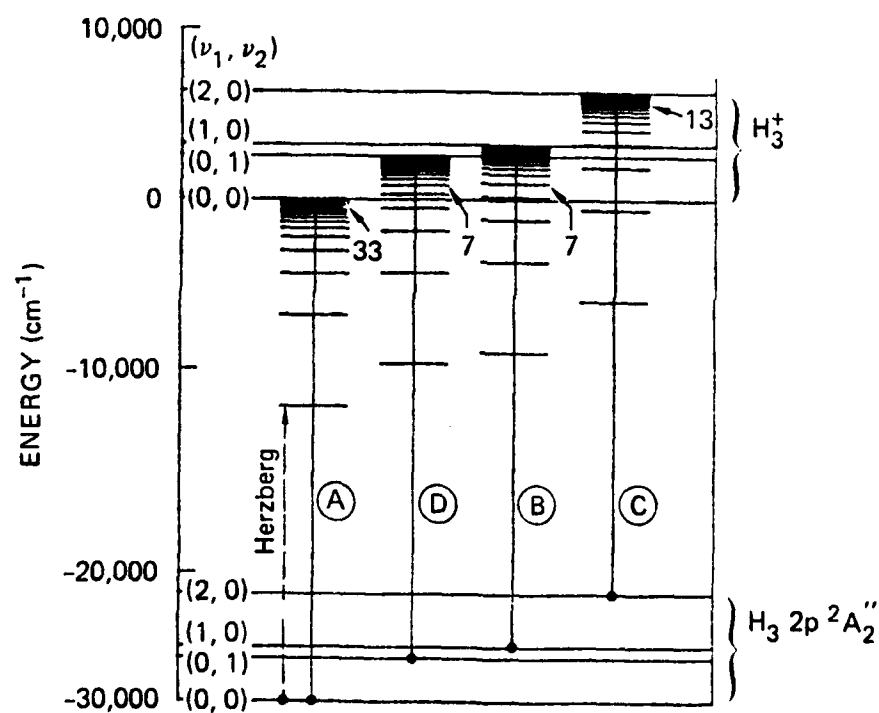
JA-330583-374E

Photoionization spectrum at high n-values

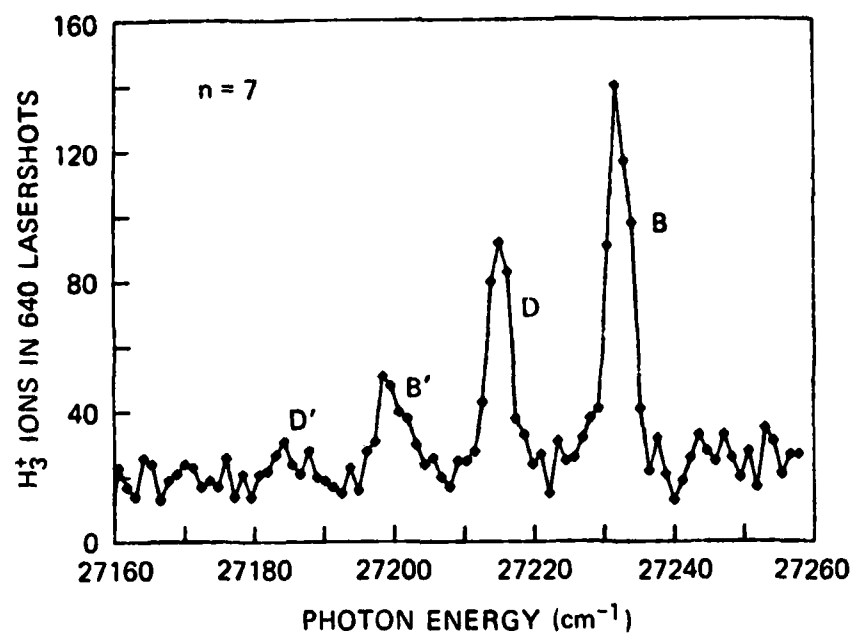


Assignment of Rydberg Series

The lowest n member observed in each series is indicated along the series ladders



Autoionization of $n=7$ states

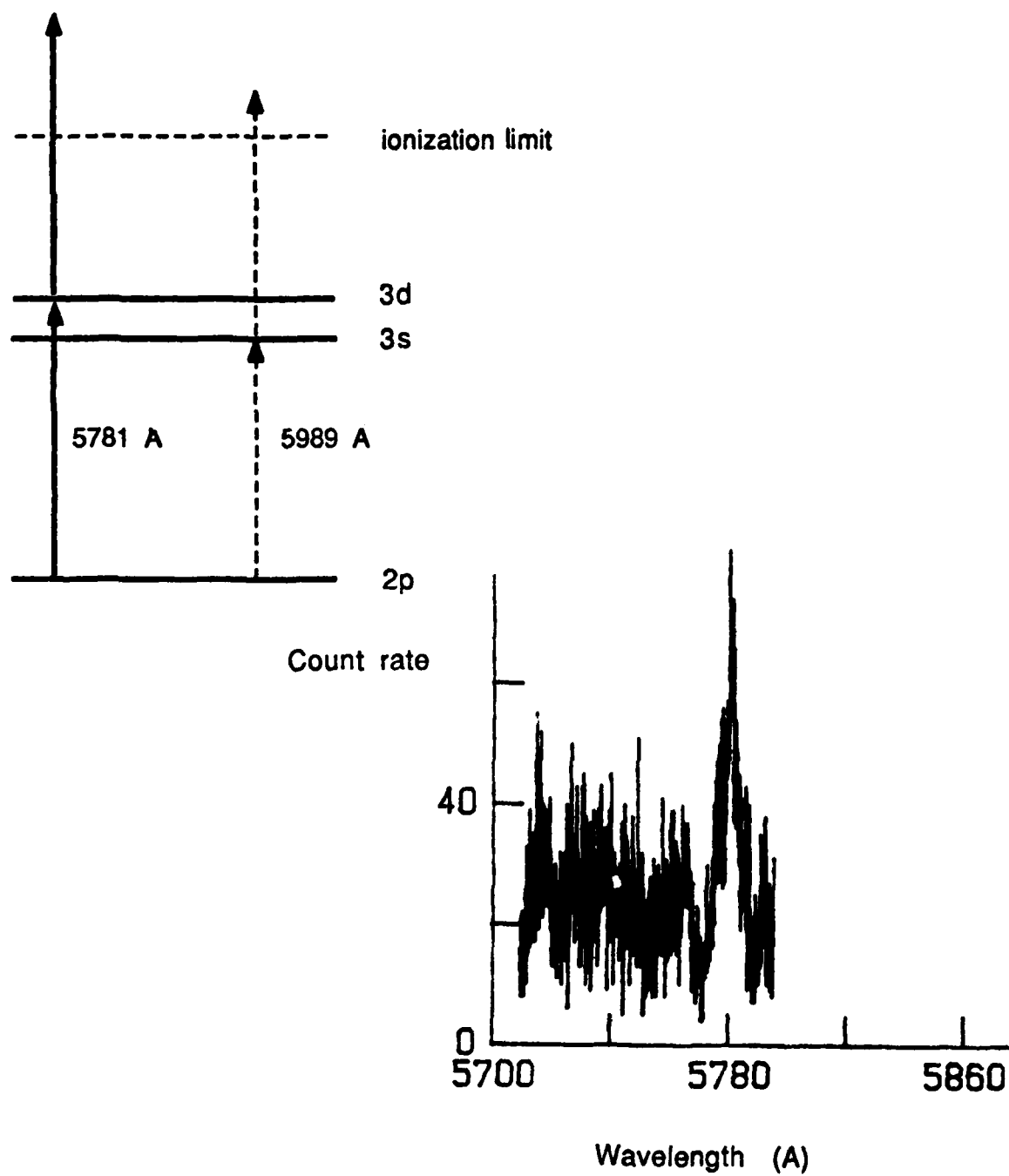


Autoionization Mechanism:

vibrationally excited core and bound Rydberg electron
exchange energy.

The peaks B and D (B' and D') are identified as transitions
to the 7d (7s) Rydberg states of vibrationally excited H_3^+ .

Two-Photon Ionization of H₃

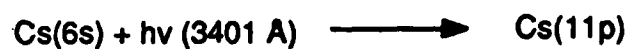


ELECTRON TRANSFER FROM EXCITED TARGET

ground state target



excitation



example of transfer from excited target

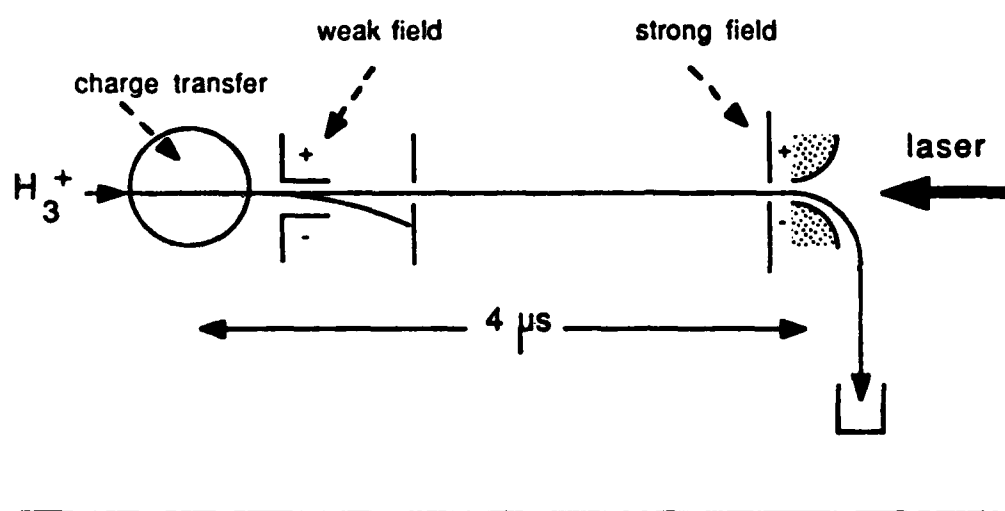


detect Rydberg molecule by field ionization



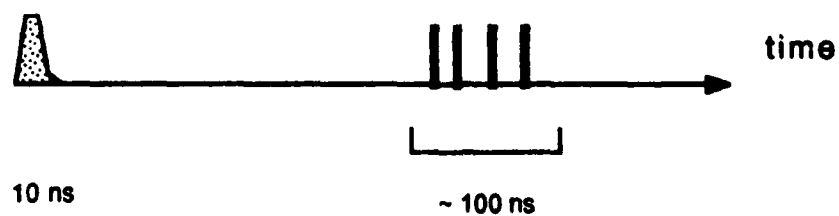
Timing

to select excitation process in charge exchange cell

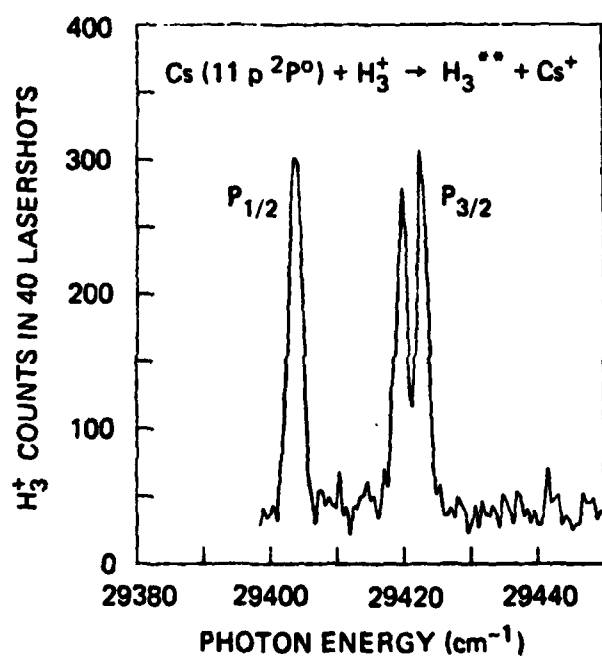


laser

arrival of ions



Excitation Spectrum of Cs



JA-7823-32

Future work

- Identify lowest autoionizing levels in the Rydberg series to support assignment of vibrational states of the metastable molecule
- Measure the linewidth of the transitions to determine the autoionization lifetimes.
- Two-Color Ionization experiments using as intermediate the $n=3$ levels observed by Herzberg to determine the quantum defects of the np and nf Rydberg series.
- Search for metastable species of the H_s molecule for which a number of metastable states have been predicted theoretically (Ref. 14).

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